Chem Ed

EDITORIALLY SPEAKING

One of the favorite winter and spring sports of chemists seems to be working for the passage of local school bond issues. An informal survey of those "what-are-you-doing-now?" conversations which bring friendships of former years up-to-date at professional meetings has revealed this not-very-surprising bit of information. Chemists as a group take their role as citizens and parents seriously. As professional men and women they not only recognize these problems but are willing to work at their solutions.

Although it is not new to find non-academic chemists talking about educational problems, it is new to find them talking so much in terms of numbers and magnitude instead of the favorite topic of recent years, quality of instruction. Our guess is that this represents no extensive pendulum swing but rather a down-to-earth realization of what is going on in our crowded classrooms across the country. It probably is typical of the kind of facing-the-facts that citizens must do everywhere. Chemists who want these facts would do well to listen to their counterparts in the schools—the chemistry teachers. Recently Samuel W. Bloom of the Science Department at Benjamin Franklin High School in Rochester put some reflections into words for readers of the Genessee Valley LSP, "CHEMunications." We quote his remarks about pupils and teachers:

> It is a normal psychological pattern for adults to dwell upon their own school experiences of a former generation. Such persons do not recognize the impact nor the significance of the changes in the size of the school population since their day. A generation ago, the high school population was relatively homogeneous, with college as the objective. Today, our public school children include the able and the less able, the physically handicapped, the mentally retarded, and the college preparatory pupil. This is the audience in the typical high school today.
>
> A teacher of science must provide appropriate experiences for all pupils. He must develop in the pupil an appreciation of the values of science, the ability to think objectively, the ability to draw valid conclusions from data, and an appreciation for the function of science as it relates to man's future welfare. Moreover, a science teacher must provide a stimulating, provocative program of studies for those pupils with science potential, pupils capable of handling the more abstruse concepts. As future citizens, our pupils will be called upon to make decisions in matters of science which may have far-reaching effects. Thus, the science teacher must develop a climate and empathy sympathetic to science in all children, a formidable task.
>
> The silhouette of the science teacher is generally vague. He is not just a physics teacher, a chemistry teacher, or a biology teacher. The science teacher must be a generalist in order to meet the needs of the present-day high school population. The science teacher should be well-grounded in subject matter without being a narrow specialist; he should have depth in one field and breadth in the others. Few schools are large enough to provide a schedule exclusively in one science; the teacher must be prepared to teach several sciences. Even if the school were large enough, it is debatable whether a teacher could lecture five straight hours per day on one subject and remain effective as a teacher
>
> Equally as important as subject matter is the ability of the teacher to communicate with his pupils. The teacher must be able both to interest and to encourage pupils in science. He must know adolescent psychology, understand and be sympathetic to children, and must be familiar with the techniques of conveying information. Without these professional skills, a teacher would prove ineffectual in the classroom.
>
> Members of the scientific community frequently try to compare high school teaching with college teaching. A valid comparison between college and high school teaching cannot be made. A college professor may have as few as nine pupil-contact hours per week. Compare this with the 25 contact hours of the high school science teacher. Moreover, the college teacher has assistants who set up the demonstrations, prepare and maintain the equipment, and clean up after each lecture. The high school teacher is on his own. He has no laboratoy assistant; he mixes his own chemical solutions; he sets up his own demonstrations; he maintains his own equipment; sometimes he even moves from room to room to meet a class.
>
> The college professor meets a group of selected individuals, selected in accord with the policy of the college. The high school teacher meets heterogeneous groups with a range of ability in consonance with the norms of the general population. When all factors are considered, the high school science teacher should be commended for any success at all in meeting the objectives of the science program.

Tomorrow's citizens are in school today. Some will decide there to become scientists: all will learn to varying degrees the place of science in the culture of today. The scientific community owes its support to those who are its educational vanguard, the high school science teachers. Quality in education need not be compromised by attacking the problems of quantity. The professional scientist can help most by keeping his goal high and his approach realistic. He can never take the place of the science teacher, even for the exceptional student. Nor can he tell the teacher what to do. He can listen, advise, and cooperate. We urge readers to join the many who are realistically getting the facts and then getting busy on programs of sympathetic support.

A ChemEd SYMPOSIUM

Educational Trends in Analytical Chemistry

Introduction

The past few decades have been a period of tremendous change in the techniques and concepts that can properly be included in the domain of analytical chemistry. It is only natural then that considerable thought and effort should be devoted to considerations of possible revisions of our undergraduate courses in this field. However, in so doing, it is necessary to consider trends in the entire undergraduate curriculum. Conversely, in considering revisions of the over-all undergraduate chemistry program, it is important to take into consideration the need of every chemist, whatever his ultimate speciality might be, for a thorough introduction to the concepts and techniques of modern analytical chemistry.

That there does not exist a unanimity of ideas as to what should be included in analytical chemistry courses or when in the curriculum they should be offered, is evidenced by the diversity of opinions expressed in the papers comprising this symposium. Part of this divergence of ideas is undoubtedly due to differences in local conditions which dictate to some extent course content as well as course sequence. Thus what is best at one school need not be right for another.

It is the purpose of this symposium to present some of the current ideas concerning the aims and obligations around which modern analytical chemistry courses should be built and to provide examples of the types of courses currently being offered at a number of schools with somewhat different local conditions. It is hoped that the papers that follow will not only provide guides for those planning revisions of their own curriculum but stimulate discussions from which better approaches to revisions of analytical chemistry courses as well as of the entire undergraduate chemistry curriculum may arise.

Richard C. Bowers, *chairman of symposium*
Northwestern University, Evanston, Illinois

EDITOR'S NOTE: The present ferment in analytical chemistry and its teaching is a repeated theme in symposia which have been held by the Division of Chemical Education and later published in THIS JOURNAL. We refer readers to those of recent years: "Teaching Instrumental Analysis," **33,** 422 ff (1956); "Qualitative Analysis—What, Why, and How?" **34,** 387ff (1957); and "An Analysis Group in an Industrial Research Organization," **35,** 2ff, 76ff (1958). Numerous other papers have presented the results of surveys, innovations in specific courses, and experimental novelties. Editorial comment has been focused on analytical chemistry courses in **35,** 53 and 587 (1958).

I. M. Kolthoff
University of Minnesota
Minneapolis

Undergraduate Courses in Quantitative Analysis

It is a truism to state that we are living in an era of revolutions: political, social, economic, and scientific, all these revolutions being interrelated. Professionally we are more concerned with revolutionary changes in science and more particularly with those in chemistry. The development of instrumentation, the discovery of new properties and the new technique based on their measurement have contributed greatly to the advancement of all fields of chemistry, both theoretical and experimental. In the last few decades we have witnessed the transformation of inorganic chemistry from a descriptive into an interpretive science. In recent years the scope of analytical chemistry has expanded enormously. It makes use of the detection and the quantitative measurement of properties and has available now a host of new properties and techniques.

The advancements in the theoretical and experimental aspects of the various fields of chemistry are accompanied by a broadening of the frontiers of the various fields of chemistry. Classical and modern physical chemistry is being practiced more and more by modern inorganic, organic, analytical, and biological chemists, while modern physical chemistry is expanding more and more in the direction of chemical physics. No specialist in a given field of chemistry can develop his field in a broad manner without making use of and being ac-

quainted with the fundamentals of the other fields of chemistry. This; of course, is the reason why we must give a well-balanced education in the various fields of chemistry to *all* chemists. When we consider the impact of the revolutionary changes in chemistry upon a modern undergraduate chemical education, we must remain constantly aware of the fact that we educate chemists and not specialists in any of the fields. The question then to be answered is: What should every chemist know and understand of inorganic, analytical, organic, and physical chemistry? A specialist in each of these fields will be tempted to overestimate the significance of his own field, and the ultimate answer can be arrived at only by a compromise among all groups in a spirit of objectivity.

Before becoming more specific I would like to state that I am not considering in any detail the year or years in which required fundamental courses in quantitative analysis should be offered or the possibility of transferring some of the laboratory work in elementary gravimetric and titrimetric analysis to general chemistry. In this respect local conditions, particularly the chemical background of freshmen students, are factors which may determine in which year or years quantitative analysis should be taken and the possibility of teaching techniques of gravimetric and titrimetric analyses in general chemistry. Dr. Swift[1] can do so at California Institute of Technology, but he and teachers at a few other colleges are in the enviable position that their select group of freshmen students has a much better background in chemistry than have freshmen in most state universities and colleges. In this connection it should be mentioned that at larger universities departments of chemistry are over-compartmentalized and that the various divisions in chemistry are relatively autonomous. Such a situation has many advantages but may consitute a handicap for attainment of the most efficient curriculum in the various fields of chemistry. For example, at the University of Minnesota the student must carry out in the freshmen course in general chemistry some semi-quantitative gravimetric and titrimetric determinations. In this course there is no time to provide instruction in accurate and precise quantitative classical techniques. A brief course in such techniques offered by analytical chemists in the beginning of the freshmen year would have the advantage that further instruction in the theory of gravimetric and titrimetric analysis and modern quantitative analysis could be postponed until the senior year when the student will have taken elementary courses in organic and physical chemistry. Moreover it does not seem rational to give instruction in the freshmen year in less accurate techniques and to teach the student in a later year the quantitative classical techniques.

One more general remark which should be of concern to all analytical chemists. In spite of the progress in modern instrumentation we still use the classical type of balances for accurate weighing. Naturally, the student must get instruction in the use of such balances, but after he has become thoroughly familiar with such balances, he should be given the opportunity to use automatic balances in his further work. Many of us have been concerned about the fact that fewer and fewer students are becoming attracted to analytical chemistry. I can fully understand that a student will not get wildly excited about laboratory work in quantitative analysis when he has to *waste* (and the emphasizing italics are mine) so much time in the balance room. Of course, availability of automatic balances would make considerably more time available for other experimental work. It seems quite possible that in ten years classical types of balances will have become obsolete and have been replaced by automatic balances.

[1] SWIFT, E. H., J. CHEM. EDUC., **35**, 248 (1958).

What Every Chemist Should Know

We will now consider briefly the question: What are—or should be—the aims and objectives of required undergraduate courses in quantitative analysis for all chemists and chemical engineers? Phrased in another way: What should *every* chemist know of quantitative analysis? Of course, there is no unequivocal answer to such a question, any more than there is to questions of minimum requirement in inorganic, organic, and physical chemistry. These minimum requirements are determined by the use most chemists make of the various disciplines of chemistry in their later lives. We should not overlook the fact that these disciplines are interrelated. It seems fair to say that a modern graduate in chemistry should have been provided with a fundamental background in the various fields of chemistry, the minimum being dictated by the requirement that he should be able to assist intelligently in the solution of problems in any of the fields of chemistry, be they of a theoretical or experimental nature or both.

Considering first minimum requirements as far as theoretical fundamentals of gravimetric and titrimetric analysis are concerned, little disagreement is expected with the statements that every chemist should have a thorough knowledge of all the factors which affect chemical equilibria, including solubility, stability of complexes, acid-base and oxidation-reduction equilibria, and that in addition he should have an understanding of the formation and purity of precipitates, of chemical and physical separations, and of errors. Some of these topics are mentioned briefly in courses in general inorganic and physical chemistry, but they are of such importance in quantitative analysis that they should be the subject of a thorough and modern treatment in introductory courses in quantitative analysis. The classical theory of titrimetric analysis in general can be presented on a modern basis. In order to understand equilibria involved in oxidation-reduction reactions, it is necessary to discuss the concept of electrode potential, the Nernst equation, and principles of potentiometric titrations. An introduction to electrochemical methods of analysis could be given, although a more extensive course in this field should be reserved for the senior year.

Fundamental Laboratory Work

As far as laboratory work is concerned, I believe that the student should have a thorough understanding of the balance and accurate weighing and of simple techniques of common operations in quantitative analysis. The first question is, how many gravimetric determinations and analyses should be carried out by the student? Most teachers interested in a modern education agree

that as a compromise the number of gravimetric determinations and analyses must be reduced drastically in order to make time available for instruction in modern techniques. A water determination, a simple gravimetric sulfate or chloride determination, and a simple analysis of a mixture containing calcium and magnesium should acquaint the student with common operations of gravimetric analysis and provide him with enough background to become further educated in later years as a specialist in gravimetric techniques and in analyzing complex material. No general agreement is expected regarding the specific gravimetric experiments to be carried out. Many analytical chemists may require at least one partial analysis of a more complex material, e.g., silica in a rock, in order to make a student appreciate the difficulties involved in an actual analysis which are not experienced in simple determinations. Quite generally it would seem desirable not to select one rigid set of experiments but to have various sets of determinations which illustrate the principles involved. Groups of students in the same class might be assigned different sets but should then be made acquainted with the work and results of the other group.

In the laboratory assignments in titrimetric analysis it would be desirable to concentrate on accuracy and illustration of principles discussed in the theoretical course. Again, every student in chemistry should not be required to make an involved analysis. Based on the general views presented above the following list of experiments is suggested, fully realizing that it would be desirable to have alternate experiments as well. After finishing the recommended set of experiments the student should have a thorough appreciation of the principles of titrimetric analysis, but he would not qualify as an experimental expert in this field. This is the way it should be, as we are not concerned with the education of specialists but of bachelors of chemistry.

Suggested Experiments in Titrimetry

Calibrate glassware.

Prepare 0.1 *N* standard solution of hydrochloric acid and of sodium hydroxide and standardize the solutions.

Determine approximately the color change interval of indicators (also of mixed indicators) with a *p*K of about 3, 5, 7, and 9. (A set of buffer solutions should be available).

Titrate 0.1 *N* acetic acid with standard base with visual end point detection (use good and bad indicators). In the same titration measure *p*H with the glass electrode and plot the neutralization curve. Compare the experimental curve with the calculated curve.

Titrate 0.1 *M* H_3PO_4 to the first and the second end point.

Determine total cations in a sulfate solution by passing over a hydrogen ion exchange resin.

Titrate an unknown chloride solution according to Mohr, Volhard, and also with dichlorofluorescein as adsorption indicator.

Titrate calcium and magnesium in the solution prepared in the gravimetric analysis of dolomite with EDTA as reagent and visual end point determination.

Prepare a standard 0.1 *N* potassium dichromate solution prepared from the pure salt. Prepare approximately 0.1 *N* permanganate and 0.1 *N* ceric sulfate and standardize against arsenic trioxide.

Determine total iron in an iron ore by reducing it quantitatively to ferrous iron and titrating with the three oxidizing standard solutions (use various indicators, improvement of end point in the titration with dichromate by adding phosphoric acid).

Standardize 0.1 *N* iodine solution against arsenic trioxide.

Standardize 0.1 *N* thiosulfate against pure potassium dichromate.

Determine copper iodometrically in a sample.

Analytical Chemistry at Minnesota

At present the University of Minnesota offers in the junior year a five-credit course in gravimetric (winter quarter) and a five-credit course in titrimetric analysis in the spring quarter. It is planned to change this as follows: Theoretical Introduction to Quantitative Analysis, fall and winter quarters, 2 and 3 credits, respectively; laboratory course in spring quarter, 4 credits.

For the senior year, when the student has taken a full year introductory course in physical chemistry, we plan to require a three-credit lecture course in the fall quarter on physical-analytical methods with main emphasis on optical and electrical methods and modern methods of separation. This is to be followed by a two- to three-credit lab course in the winter quarter in which the student carries out spectrophotometric experiments, including a check of Beer's law, differential spectrophotometry, spectrophotometric titration, infrared analysis, fluorometric analysis, and flame spectrophotometry. In electroanalytical chemistry he carries out a potentiometric, conductometric, amperometric, and coulometric titration, a controlled potential electrolysis of copper and lead in brass, and a simple voltammetric experiment. Finally, separations are made based on extraction and various types of chromatography. These senior-year courses are not intended for graduate students majoring in analytical chemistry. They will be offered the modern subjects in considerably greater detail than is done in the above courses.

An elective course on Analysis of a Complex Material (3 credits), which is intended for graduate students majoring in analytical chemistry, is recommended to seniors who are interested in analytical chemistry.

Deadlines for Programs of NSF-SPISE

July 25, 1960—Undergraduate Education in Science and Engineering
July 31, 1960—Research Participation for College Teachers
August 8, 1960—Summer Training for Secondary School Students
August 8, 1960—Research Participation for High School Teachers

Applications for project support in all these programs should be addressed to Special Projects in Science Education Section, NSF, Washington 25, D. C.

James S. Fritz
Iowa State University
Ames

Educational Trends?

What They Are and What They Should Be

Analytical chemistry has come a long way from the "cookbook" subject it used to be. Also, there has been a growing recognition of the value and importance of analytical chemistry and analytical chemists. Analytical chemistry is important to chemistry students not only for its practical value, but also because more than any other subject it brings together the chemical reactions and principles learned in inorganic, organic, and physical chemistry.

In recent years there has been a tremendous development of analytical methods and techniques. This makes it desirable for us to take a critical look at instruction in analytical chemistry to see whether we are keeping up with the times and meeting the challenge that such rapid change brings. At the same time it is important not to neglect the discipline that quantitative analysis has traditionally demanded, or to be carried away with novel methods of analysis that in retrospect are only of trivial value.

Survey of Educational Trends

In order to discover some of the existing trends in teaching analytical chemistry, a questionnaire was sent to 50 analytical chemistry professors in various colleges and universities throughout the United States. Information was requested on the present content of undergraduate courses and on recent changes in the emphasis given to various topics. Comment was invited regarding the professors' attitudes on educational trends. Replies were received from 79% of the professors. Approximately 73% of the replies received were from medium-sized or large schools, and the remaining 27% were from small schools.

In replies from 33 schools, a majority of students had only freshman chemistry (usually with some qualitative analysis) before taking the elementary quantitative analysis course or course sequence. However, 21% of the replies reported that most or all of their students had taken some organic chemistry before quantitative analysis, and 9% reported that their students had some physical chemistry before quantitative analysis. In virtually all elementary quantitative analysis courses, either 2 or 3 hours per week are spent in classroom work, the average being 2.5 hours. An average of 7.0 hours per week is devoted to laboratory work. The average duration of the elementary analytical course sequence is 75% of the regular school year.

Table 1 lists some of the topics included in elementary quantitative analysis courses. It is interesting to note that a large majority of courses include complex-formation titrations, statistical treatment of errors, electrodeposition, and colorimetry. In Table 2 the average time spent on various topics in elementary quantitative analysis is tabulated. In most courses not more than one class period is spent on each of the newer techniques such as EDTA titrations, ion-exchange, and solvent extraction.

Table 1. Study of Topics Included in Elementary Quantitative Analysis at 28 Schools

Topic	% of schools including topic
Complex formation titrations	96
Statistical treatment of errors	93
Electrodeposition	89
Colorimetry, photometric methods	86
Colorimetry, visual methods	75
Instrumental analysis	68
Ion-exchange in analysis	68
Solvent extraction	50
Chromatography	43
Gas analysis	36
Organic functional group methods	25
Other	36

The advanced course offerings in analytical chemistry are tabulated in Table 3. Of the schools surveyed, all but three small schools offered a course in instrumental analysis. A majority of the universities also offer at least one other advanced analytical course. Although fewer schools offer separate courses in organic quantitative analysis, emission spectroscopy, and the like, a larger number consider these topics in other advanced courses.

Table 2. Average Time Spent on Various Topics in Elementary Quantitative Analysis Courses at 29 Schools

Topic	% of Course*
The balance and weighing	4
Calibration of weights or glassware	3
Gravimetric analysis	23
Titrations involving precipitate formation	6
Acid-base methods of analysis	18
Oxidation-reduction methods	18
Complex formation titrations	4
Colorimetric methods	7
Separations using solvent extraction	3
Ion exchange in analytical chemistry	3
Chromatography	2
Instrumental analysis (polarography, spectrography, etc)	5
Gas analysis	3
Statistical treatment of errors	4

* % of course was calculated only for courses that include the topic. Few courses included *all* of the above topics.

An idea of some of the trends in teaching elementary quantitative analysis can be obtained by noting some of the topics that have recently been added or given

Presented as part of the Symposium on Educational Trends in Analytical Chemistry, sponsored jointly by the Divisions of Analytical Chemistry and Chemical Education, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

Table 3. Advanced Analytical Course Offerings of 32 Schools

Course area	% of schools offering course
Instrumental analysis	91
Advanced anal. chemistry including special topics courses	81
Micro analysis	34
Emission spectroscopy	16
Organic quantitative analysis	9

increased emphasis, and also the topics that have been dropped or de-emphasized. This information is summarized in Table 4. These data show that in most courses less time is now being spent than formerly on gravimetric analysis and certain other "classical" methods of analysis. Increased attention is being paid to the use of instruments in analysis, complexometric titrations, colorimetry, and the like.

Table 4. Trends in the Content of 28 Elementary Quantitative Analysis Courses

Topic	% of schools giving topic added emphasis	% of schools giving topic decreased emphasis
Instrumental analysis	50	..
Complexometric titrations	39	..
Colorimetric methods	36	..
Separations	29	..
Statistics	25	..
Ion exchange	18	..
Solvent extraction	14	..
Electrodeposition	14	..
Organic analysis	11	..
Gravimetric analysis	..	64
Other "classical" techniques	..	29
Details of methods	..	14

A number of timely comments were received from professors who replied to the questionnaire. The essence of some of these comments, many of which were repeated by several persons, is given below.

For the vast majority of present-day students, the old philosophy of a rather extensive gravimetric training is outmoded.

Organic chemistry should be taught before analytical. If possible some physical chemistry should also precede analytical.

More quantitative analytical measurements should be made in freshman chemistry laboratory.

Laboratory skills are being badly neglected.

More emphasis should be placed on principles and theory, less on descriptive material.

Use more instruments in the elementary quantative analysis course, but keep instrumental analysis as a separate course. Do not dilute the fundamental analytical course with too much instrumental.

Quantitative analysis laboratory should be made more interesting. Less emphasis should be placed on unknowns with set procedures.

Sponsored research threatens teaching standards by taking the better graduate students from teaching duties.

Qualitative analysis is still an analytical course and should receive more emphasis.

There is so much material to cover that it is difficult to know what to emphasize.

There is little interest in improving courses in any fundamental way because it is not personally rewarding to do so.

Summary of Trends

Place of analytical chemistry in the undergraduate curriculum. There is a definite movement toward teaching organic chemistry before quantitative analysis. There is also an inclination to teach some physical chemistry before quantitative analysis. Analytical chemistry is now a more sophisticated subject than it used to be and should be treated as such. There is also a trend toward more quantitative work in the first year of college chemistry. This would be especially helpful if the regular quantitative analysis course is being postponed until the junior year.

Content of elementary quantitative analysis course or sequence. In most schools there is a definite reduction in emphasis on gravimetric analysis. Many are also devoting somewhat less attention to certain other "classical" techniques. However, all courses are retaining the fundamentals of gravimetric analysis. Many are merely cutting down on the descriptive parts and are reducing repetition.

In a majority of cases, topics such as EDTA titrations, colorimetric methods of analysis, statistics, and ion exchange are being added or are being given increased emphasis.

There has been a rapid expansion in the theory and methods of analytical chemistry, but the time available in analytical courses has not increased. To combat this problem, the trend is to emphasize principles and to cut down on descriptive and "cookbook" analytical chemistry.

There is more discussion of instrumental methods in elementary courses. Use of instruments such as *p*H meters and photoelectric colorimeters in laboratory is more widespread.

Advanced analytical courses. Except for small schools, virtually all schools offer a course in instrumental analysis. Many schools (81% of those surveyed) also offer a course on advanced chemical methods of analysis or on special topics. Quantitative organic analysis has been largely ignored until recently, but many of the larger universities are now introducing courses on this important aspect of analytical chemistry.

Comments on Educational Trends

The dominant trend in analytical chemical instruction is one of cautious change. These changes, which are summarized above, are in the right direction and are encouraging. However, it is the author's feeling that many professors are being overly cautious and that modernization of undergraduate analytical courses is proceeding too slowly.

Writers of textbooks have been especially conservative. In most books, important and proved analytical techniques such as complexometric titrations with EDTA, ion-exchange, and solvent extraction are treated briefly if at all. Quantitative analysis remains almost exclusively inorganic in nature. No "boldly different" elementary quantitative analysis text has been written. Conformity to convention seems to be the keynote of most authors.

Although some progress is being made, inclusion of quantitative organic analysis in course offerings is still lagging. This is an important deficiency, because organic analysis is now of equal or greater practical importance today than inorganic analysis. While some of the principles learned in inorganic analysis are directly applicable to organic analysis, many aspects of organic analysis are unique.

A separate course in organic analysis is one answer to this problem. However, the situation also can be improved by incorporating some organic analysis into existing courses. For example, nonaqueous titrations, quantitative determination of carbonyl compounds by oximation, alcohols by acetylation, and esters by saponification could be discussed with acid-base theory and practice. Ultraviolet spectrophotometric determination of organic compounds could be included when the subject of inorganic spectrophotometry is considered.

Finally it should be recognized that the laboratory part of many quantitative analysis courses should be revised. The unknowns now done in laboratory are repetitious; they bore the students and do not provide very efficient instruction. Each experiment done in laboratory should illustrate a different principle or technique. Laboratory work does not have to consist entirely of analyzing unknowns. Where possible, more emphasis should be placed on the student's finding appropriate procedures for himself and applying them to actual samples.

W. B. Thomas
Bates College
Lewiston, Maine

The Modernization of Analytical Chemistry in a Liberal Arts College

The age of science in which we live is full of stresses and strains resulting from the high rate of discovery in science and technology. It is therefore not surprising to find science education in a state of flux; the course content and methodology of science teaching are being examined by many groups and individuals. In the field of chemistry there is considerable searching for improved presentation of the subject all the way from the high school course on through graduate study.

Analytical chemistry has undergone a veritable revolution during the last thirty or forty years, and it is essential that educational institutions keep in step with new developments in the field. This poses a number of problems that are especially critical for a small liberal arts college. It is the purpose of this paper to discuss these problems and to suggest solutions for some of them.

When changes in the curriculum of a liberal arts college are under consideration, it is usually necessary to think in terms of substitution rather than addition. That is, it is seldom possible simply to add new courses because of staff limitations and also because there is usually a ceiling applied to the number of courses a student may take in his major field. Indeed, there is considerable pressure at the present time to reduce the offerings in the various departments. If, then, a new course is to be introduced, it must replace one already in existence and the change must be evaluated by considering not only the gains obtained from the new course but also the losses resulting from the elimination of the old one.

Presented as part of the Symposium on Educational Trends in Analytical Chemistry, sponsored jointly by the Divisions of Analytical Chemistry and Chemical Education, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

Several years ago the offerings in analytical chemistry at Bates College were revised with two main objectives: (1) introduce a course in instrumental methods of analysis; and (2) make room for a course in advanced inorganic chemistry. A comparison of the new and old curricula is given in the table.

Comparison of New and Old Curricula at Bates College

	Old		New	
	First semester	Second semester	First semester	Second semester
I	General	General	Gen. & Qual.	Gen. & Qual.
II	Qual.	Intro. Physical	Intro. Quant.	Intro. Phys.
III	Quant.	Quant.	Intermed. Quant.	Instrum. Methods (Lab only)
	Organic	Organic	Organic	Organic Inorg. (Class only)
IV	Physical Adv. Organic	Physical Adv. Organic	Physical Adv. Organic	Physical Adv. Organic

Lower Level Courses

Possibly our most basic decision was to move qualitative analysis into the freshman year. We could have introduced some instrumentation into the year course in quantitative analysis without changing the curriculum (we actually did this for two years), but there would have been no room for an advanced inorganic course. Also we felt that the introduction of qualitative analysis would strengthen the freshman course. This assumption has been substantiated by experience. We run the qualitative analysis throughout the year, interrupting it at appropriate times to introduce general chemistry experiments which are mostly quantitative in nature. We like this arrangement which we believe is unique. On the other hand,

the dropping of the separate qualitative analysis course has definitely resulted in some losses. Chief among these is what I like to call "chemical horse sense." The ability to predict the nature of a chemical reaction and to represent it by means of an equation is best acquired by the type of drill that is possible in a course in qualitative analysis. This type of training has almost disappeared from chemical education in this country and constitutes a real loss.

The introductory quantitative analysis which replaced qualitative is a conventional course comprising five volumetric and two gravimetric analyses. It is a service course which is taken by many students majoring in other sciences in addition to our chemistry majors. It obviously has strengthened the laboratory work in the introductory physical chemistry course which is given in the second semester of the sophomore year. We feel that we now have an excellent premedical sequence without giving any special premedical courses. In fact, this change enabled us to drop a premedical analysis course which formerly was given but is not shown in the table.

It is worth noting that we have chosen to retain a conventional introductory quantitative analysis course in the sophomore year and to introduce modern developments in the junior courses. There is some question regarding the wisdom of this decision in view of the fact that many of our students, including most premedical students, do not take the advanced courses. We may eventually decide to include some instrumental methods, for example, colorimetry, in the introductory course.

Upper Level Courses

The laboratory work in the intermediate quantitative course in the first semester of the junior year provides the opportunity to introduce analyses of a varied nature including some involving organic compounds. Included in the latter category are saponification and iodine values on an oil, chlorine, or sulfur in an organic compound and a semimicro Kjeldahl determination. We hope to add at least one functional group analysis to the assignments in the near future. We consider it highly desirable to give our students some contact with organic quantitative analysis. Plans are now being laid to introduce some problem-type analyses into the course. The student will do a literature search and make his own decision as to the method of analysis to employ.

The class work in this intermediate course is devoted largely to the theory of instrumental methods of analysis in preparation for the laboratory work in this field which comes in the second semester. This arrangement, which is probably unique, solves the knotty problem of covering the theory of an instrument before it is used in the laboratory. With only one instrument of a type available, it is necessary to arrange a rotating schedule which cannot be synchronized with the class work if class and laboratory are presented concurrently. Obviously the first semester course must be a prerequisite for the second which may present a problem in some instances. We are well satisfied with the arrangement after four years of experience with it.

The laboratory course in instrumental methods (second semester) includes potentiometric, conductometric, and amperometric titrations, a Karl Fischer moisture determination, a gas analysis and work in spectrophotometry (visible and ultraviolet) colorimetry, polarography, flame photometry, and paper chromatography. We expect to expand and diversify the assignments as more instruments are acquired.

In concluding this discussion of the curriculum I would like to stress the point that our main objective has been to teach chemistry and not analytical procedures or instrumentation. We do not discuss electronics, preferring to stress the chemical principles involved in the use of the instrument.

Financial Problems and Solutions

The introduction of a course in instrumental methods of analysis obviously presents financial problems in addition to the curricular ones just discussed. Most colleges find it difficult to include in their regular budget items costing from several hundred to several thousand dollars. Fortunately there are ways of getting around this problem, and I would like to discuss a number of solutions that we and others have employed.

It frequently happens that an individual or group of alumni would like to make a gift for something tangible. One of our instruments bears a brass plate attesting to the fact that it was a gift from one of our older classes.

Industrial laboratories represent another source of instruments for a college. An instrument that has been replaced by a newer model is often quite suitable for instructional purposes. Sometimes the replaced instrument can be obtained directly from the company perhaps through the aegis of an alumnus who works there. Or the instrument may be obtained through a laboratory supply house or directly from the manufacturer.

In recent years chemical companies and others in related fields have taken cognizance of their stake in science education and are supporting it in various ways. Many colleges have used grants from companies to purchase instruments that they would have found difficult to obtain in any other way.

Another source of funds and one that may become increasingly important during the next few years comprises the governmental agencies and private foundations that are supporting research. At the present time most grants are made for a research project which frequently requires the purchase of an instrument for a specific purpose. As a result, most of the grants have gone to the universities with their well-established research programs. On the other hand there is increasing recognition of the need for supporting science teaching in liberal arts colleges.

The writer had the privilege of attending in June the Wooster Conference on Teaching and Research in the Liberal Arts College sponsored jointly by the National Science Foundation and the Division of Chemical Education. At this conference a thorough study was made of ways of encouraging research and creative teaching in liberal arts colleges. Obviously financial considerations received much attention as indicated by attendance at the conference of representatives of most of the foundations and agencies. The report of

the conference has been sent to the chemistry departments of all colleges in the country and merits careful study by all who wish to upgrade their departments.

Other problems primarily financial in nature such as the upkeep and obsolescence of instruments are serious but usually can be handled once the instrumentation course becomes established. It is possible for a liberal arts college to incorporate a reasonable spectrum of modern methods into the courses in quantitative analysis, and it seems to be imperative that this be done.

Ernest H. Swift
California Institute
of Technology
Pasadena

Quantitative Analysis Versus Quantitative Chemistry

One of the most promising trends in connection with the undergraduate instruction in chemistry has been the recent widespread willingness to reexamine the various courses of the curriculum with regard to their objectives, values, and proper sequence and to apply the experimental method in this examination.[1] This symposium is an example of the trend and presents an excellent opportunity to take advantage of this willingness, first, to examine the current objectives of the conventional undergraduate courses in quantitative analysis, and secondly, to question whether these objectives are valid in view of present developments and conditions. If these objectives are not valid, then one can ask what they should be, how courses can be modified to meet these objectives, and at what stage in the curriculum they should occur. Otherwise stated, is there a trend at present and is it proceeding in a desirable direction?

Upon looking at the historical development of the older fields in science or engineering, one notes a strong tendency for the instruction in a field to follow the chronological development of that field. Also, on looking back one perceives that at times this tendency has been so strong that it has, at least for a long time, inhibited objective appraisals of the instruction in these fields. An example of this is seen upon looking back at the undergraduate curricula in chemistry prevailing during the early part of this century. The freshman course was very largely descriptive in nature; the work of the second year usually started with qualitative analysis and ended with quantitative analysis; the organic course occupied the third year; and a course in physical chemistry did not appear until the senior year. At this time such topics as fire assaying, and water and gas analysis were commonly found in the upper or graduate years. Consequently, from one quarter to one third or more of the total time given to the chemistry curriculum was occupied by analytical courses.

The Situation Fifty Years Ago

In the early 1900's one could find justification for this situation because a considerable proportion of the students majoring in chemistry completed, or rather terminated, their training with a bachelor's degree. Thereafter they went to work in control or analytical laboratories and made extensive professional use of their analytical training. As a result of this situation, the analytical courses tended to be essentially procedural in nature, and the laboratory work was devoted primarily to the learning of various techniques.

There seems justification for stating that this tendency has persisted in analytical courses to the present time with two major trends having taken place. The first of these trends was the placing of more emphasis on the application of principles, and two authors and their texts should be mentioned in this connection. The first of these was Professor Stieglitz and his two-volume qualitative analysis text,[2] and the second was Professor Fales and his text on quantitative analysis.[3] The second trend has been the increased attention paid to instrumentation, and this has been so pronounced that at the present time courses in instrumental analysis have gradually replaced the specialized courses in such topics as water and gas analysis previously given. The two authors mentioned above should be given great credit for their effective pioneering efforts in broadening the scope of the analytical courses. However, there is still great emphasis on quantitative analysis per se both in the courses as they are given and in the texts as they are written. Upon reading the prefaces and introductions of the majority of modern quantitative texts, one detects what may be a subconscious uneasiness in this regard which results in a general effort to justify and to point out the importance of quantitative analysis. For example, one modern text spends the first five pages on the importance and scope of quantitative analysis.

[1] See, for example, THIS JOURNAL, **34**, 365, 419 (1957) and **35**, 164ff, 246ff (1958).

Presented as part of the Symposium on Educational Trends in Analytical Chemistry, sponsored jointly by the Divisions of Analytical Chemistry and Chemical Education, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.
Contribution No. 2537 from the Gates and Crellin Laboratories of Chemistry.

[2] STIEGLITZ, JULIUS, "Elements of Qualitative Chemical Analysis," The Century Co., New York, 1911.

[3] FALES, H. A., "Inorganic Quantitative Analysis," Appleton Century-Crofts, Inc., New York, 1925.

The Situation Today

But even if one grants all of the claims made regarding the importance and scope of quantitative analysis, is there justification today for spending as much as one quarter of the total undergraduate curriculum on this one subject? Even looking at this question as an analytical chemist, this justification seems difficult. Today, contrary to 50 years ago, relatively few chemistry graduates are going to be engaged in work which is predominantly analytical in character. And today most of the control and analytical work has become so routine, or so automated, that trained chemists are no longer required to carry out the technical manipulations of control and analytical processes.

However, one of the predominant trends in both science and engineering during the last 25 years has been a progressive increase in the quantitative nature of these fields, both theoretically and experimentally. As a result, there is an increased need on the part of students majoring in the various fields of science and engineering for an appreciation of, and some experience in, the problems involved in designing, performing, and critically interpreting quantitative experiments. And of equal importance, there is need for a realization by present-day students that progress in science and engineering is still dependent upon the experimental method.

Therefore, we are faced with the problem of trying to cope with two conflicting trends—first, the decrease in the professional value of quantitative analysis per se, and, secondly, the increased need on the part of scientists and engineers in general for a proficiency in quantitative experimentation. As an attempt to meet this situation, the proposal is made that we begin by a reorientation of the objective or objectives of our basic quantitative analysis courses. Just as qualitative analysis is no longer given for its professional value, but because it is uniquely effective for teaching systematic inorganic chemistry, I would propose that the basic quantitative analysis course be used first, to give a training in quantitative measurements, second, to illustrate the use of mass action principles in the control of typical chemical reactions, and third, to provide a representative background of factual general chemistry.

Quantitative Chemistry for Freshman Students

The next question which arises is where in the curriculum should this course be taught? I would propose that for both science and engineering students who have had high school or preparatory school chemistry the logical place is the freshman year and that this basic training in quantitative measurements become the major part of the laboratory work of the general chemistry course. There are various justifications for this proposal. First, an increasing number of students, especially those with an interest in science and engineering, are taking preparatory school courses in chemistry, and there is evidence that the quality of these courses has begun and will continue to improve. As a result, students having had such courses are bored with the conventional general chemistry laboratory work. Secondly, the general chemistry course is usually the only chemistry course which many science and engineering majors will be required to take. Finally, I firmly believe that the sooner students learn to approach science and engineering quantitatively, both theoretically and experimentally, the better prepared they are for their subsequent professional studies, regardless of their nature.

An experimental freshman course based on these considerations has been in progress for the past three years at the California Institute of Technology and, although a description of the laboratory work of this course has been given previously,[4] I shall briefly review our reasons for initiating it, the general nature of the work, and shall then attempt to assess the results to date.

Before beginning, I should state that the curriculum of the freshman year at the California Institute is uniform for all students and that essentially all have had courses in chemistry and physics and four years of mathematics. Even before World War II, and especially since then, there was increasing evidence that the laboratory work of our freshman chemistry course was neither stimulating the interest of the students nor holding whatever previous interest they may have had. Part of this evidence was a continuing decrease in both the number and quality of the students electing to major in chemistry or chemical engineering after the freshman year. An effort had been made to introduce so-called quantitative experiments into this laboratory work, but apparently neither the instruments provided nor the exyerimental skill required was such as to challenge or interest the students. Accordingly, three years ago a substantial portion of our basic quantitative analysis course, formerly given in the sophomore year to majors in chemistry and chemical engineering, was shifted into the first two quarters of the freshman course. (The work of the third quarter continued to be qualitative analysis, carried out on a semi-quantitative basis.) Although the nature of the experiments and the standard of the measurements required remained essentially the same as formerly, a conscious and persistent effort was made to convince the students that the objectives of this laboratory work were not to train analysts but to give them training in carrying out measurements of fundamental physical quantities, and in criticizing and evaluating these measurements. While these measurements were applied to chemical systems, it was stressed that they were measurements that any experimental scientist or engineer might be required to make in his subsequent professional career.

There has been continuous experimentation toward obtaining diversification of these measurements. As a result, the experiments now not only include measurements of mass and of volumes of liquids, but also volumes of gases; calibrations involving the conversion of an apparent weight in air of a liquid to the corresponding volume at a different temperature; electrical potential, current, and total quantity of electricity by constant current-time measurements (coulometric titrations); and light measurements (colorimetric determinations). Furthermore, the chemical systems and reactions involved are selected, not because of their analytical interest, but to illustrate typical mass action principles and types of chemical reactions. I am of the opinion that the success of this type of work will

[4] THIS JOURNAL, 35, 248 (1958)

be largely determined by the extent to which we succeed in adopting these objectives and in convincing the students that these are our objectives. In other words, how successful are we in justifying the title of Quantitative Chemistry, rather than Quantitative Analysis, which we have given to this course?

Educational Advantages

An objective evaluation of the success of this laboratory work is difficult. However, we believe that several constructive results have been obtained and the course is being continued. First, there has been a dramatic improvement in the application and apparent interest of the students. This seems to have resulted in part from the fact that they are challenged by the opportunity of using good equipment to its full capacity, of testing the capabilities and limits of their instruments, and of testing their proficiency against professional standards by means of the unknown. Next, as a result of this course, all of our students now obtain a basic training in quantitative measurements regardless of what field of science or engineering they may enter. At the same time, the progress of students intending to major in chemistry or chemical engineering has been accelerated by approximately two-thirds of a year. This permits them to take undergraduate research or more advanced and specialized courses in their junior and senior years. Also, after the first year there was an increase of approximately 60 per cent in the number of students electing to major in chemistry and chemical engineering, and this gain has been maintained in the succeeding years despite the recent increase in the proportion of students majoring in physics and mathematics.

Mention should be made also of the fact that after the introduction of the quantitative work into the first two quarters of the freshman year, there was a very pronounced improvement in the character of the work of the qualitative analysis course of the third term. This applied both to the laboratory work and to the general appreciation of the principles involved.

Last year a special freshman course with laboratory work of essentially the same character was given to a selected group of 25 freshmen at the University of California at Los Angeles. On the basis of the results obtained the course is being continued this year and the number of students admitted has been approximately doubled.

It seems evident that because of the increased interest in science and engineering which has occurred since Sputnik I, and because of the various efforts which are being made by the National Science Foundation and other agencies to improve the content and quality of the high school courses in physics, chemistry, and mathematics, there will be a marked increase in the number of students entering college with preparation which will qualify them to take freshman courses such as those being given at the California Institute and at the University of California at Los Angeles. Thus it seems that by a trend from quantitative analysis toward quantitative chemistry the possibility exists of giving qualified engineering and science majors a better background in quantitative experimentation and at the same time of substantially expediting the progress of our chemistry and chemical engineering majors.

International Union of Pure and Applied Chemistry Recommendations

During the Twentieth Conference of the I.U.P.A.C., which was held in Munich in August, 1959, the Committee of the Analytical Chemistry Section discussed certain points of confusion in the literature. Recommendations were made as follows:

Notations of Indicators in Titrimetric Analysis. Many dyestuffs have been recommended as indicators in chelatometric and redox titrations, and a host of trivial names often exists for the same compound. Examples can be found in the literature of a compound having been recommended as a new indicator because it has a different name when the compound has, in fact, been in use for years under a different name.

To avoid future confusion and embarrassment of authors and editors, the Committee recommends that when a dyestuff is proposed as an indicator in any type of titration, and particularly when it is claimed as new, the British Colour Index or Schultz Number be quoted along with the trivial name.

Terminology of Complexing Agents. Because of the existing confusion regarding terminology in the use of complexing agents as titrants, the Committee tentatively recommends the use of the following terms until such time as further action is taken.

(a) The group of polyamino-polycarboxylic acids which form *anionic* complexes shall be termed "complexans."

(b) Titration processes in which any type of complexing titrant is used shall be termed "complexometric titrations."

(c) Those complexometric titrations which involve titration with a chelating agent shall be termed "chelatometric titrations" and represent a special type of complexometric titration.

Louis Meites,
Joseph Steigman,
and **C. H. Liu**
Polytechnic Institute of Brooklyn
Brooklyn, New York

Undergraduate Analytical Chemistry:

An integrated sequence

The heart of the undergraduate curriculum in chemistry at the Polytechnic Institute of Brooklyn is outlined in Table 1. It includes four courses in analytical chemistry. The first two constitute a full-year sequence, required of all chemists, chemical engineers, and metallurgical engineers in their sophomore year. Prior to the development of the approach described in this paper, one semester of this course had been devoted to classical qualitative analysis, and the other had been devoted to gravimetric and volumetric methods of quantitative analysis. The third is a one-semester course, required of each chemist in the second half of his junior year, following a year of organic chemistry and a semester of physical chemistry of which thermodynamics is the principal subject. This course is concerned with the so-called "instrumental" methods of research and analysis. The fourth is an elective one-semester course in nuclear chemistry which can be taken in the senior year. However, students who are particularly interested in analytical chemistry may, with special permission, be admitted to one of the graduate courses, including radiochemistry, offered by the analytical division.

Table I. The Chemistry Curriculum at the Polytechnic Institute of Brooklyn

Year	Semester	Courses in chemistry	Courses in related subjects
Freshman	1, 2	Structure of Matter[a]	Mathematics I, II (mathematical logic, analytic geometry, calculus)[a] Physics I, II (statics, dynamics, heat, electrostatics, magnetism)[a]
Sophomore	1	Analytical Chemistry I[b]	Mathematics III (determinants, theory of functions, linear differential equations) Physics III (AC circuits, geometric optics)
	2	Analytical Chemistry II[b]	Mathematics IV (vector methods, partial derivatives)
		Organic Chemistry I[c]	
Junior	1	Organic Chemistry II[c]	Mathematics V (infinite and Fourier series, partial differential equations, probability theory)
		Inorganic Chemistry	
		Physical Chemistry I[b]	
	2	Analytical Chemistry III	
		Physical Chemistry II[b]	
		Qualitative Organic Analysis	
Senior	1	Thesis I	Atomic Structure I
		Physical Chemistry III	Chemical Engineering Technology
	2	Thesis II	Atomic Structure II
		Elective[d]	

[a] Required of all students at the Institute regardless of major field.
[b] Required only of students majoring in chemistry, chemical engineering, or metallurgical engineering.
[c] Required only of students majoring in chemistry or chemical engineering.
[d] See text.

A thesis based on a program of original research carried out during the senior year is required of all students majoring in chemistry, and this forms an important part of the training in analytical chemistry of any student who elects to carry out a research program in that field.

This paper contains summaries of the philosophy and organization of each of these offerings, and outlines the reasons for our conviction that they constitute one very effective solution to the problems confronting undergraduate education in analytical chemistry today. In the design of each of these courses, an effort has been made to achieve the highest possible degree of integration with previous or concurrent courses. By stripping out much dead wood that has accumulated in the analytical curriculum over the decades, it has been possible to include a large amount of thoroughly up-to-date material which gives the student a good understanding of the present status of the field and a good background for further work in it. Our belief that college-level institutions should endeavor to teach analytical chemistry rather than chemical analysis—to teach the principles of a science instead of describing the present (or past) state of a craft—has led to a heavy stress on fundamental theoretical principles rather than on specific technical applications.

Aims of Qualitative and Quantitative Analysis

The aims of the first-semester sophomore course in qualitative analysis appear to us to be of two kinds. The real aims are to give the student a sound, thorough, and systematic exposition of descriptive inorganic chemistry, and to give him a good working knowledge of the principles of chemical equilibrium and their applications. The first of these is shared to some extent by freshman courses and by advanced courses in inorganic chemistry, but the second enters into no other course in the customary undergraduate curriculum. Few chemists, and probably no analytical

Presented as part of the Symposium on Educational Trends in Analytical Chemistry, sponsored jointly by the Divisions of Analytical Chemistry and Chemical Education, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

chemists, would question the importance of achieving both.

Unfortunately, these real aims of the qualitative analysis course seem to be largely obscured by the ostensible aim of teaching a scheme for the detection of any of a number of "common" cations or anions in a mixture. Many charges have been leveled against this ostensible aim, and these need hardly be repeated here. The havoc which is wrought on any of the common schemes by the introduction of a few other substances—which may be both more common and more important than the ones included—would alone prompt a suspicion that the game is hardly worth playing. Even the truly comprehensive scheme of Noyes and Bray[1] no longer constitutes a realistic approach to qualitative inorganic analysis in these days of the flame photometer, the emission spectrograph, the polarograph, and the host of other weapons that can be brought to bear on the problem of detection and identification. On such grounds it appears that any rigidly formalized scheme of group separations and confirmatory tests amounts to little more than a series of more or less arbitrarily arranged exercises in test-tube chemistry. As such it has little relevance to the facts of life in the present-day analytical laboratory, less permanent value to the student, and practically no interest whatever for the increasing number of students who detect its lack of reality. What is worse, it gives the student little opportunity to discern the manner in which the scheme was constructed, little insight into the thought processes employed by the analytical chemist, and almost no chance to develop his own ability to proceed independently from observation to inference and further experimentation in an orderly and logical fashion.

These reasons have led a number of institutions to drop qualitative analysis from their curricula without further ado, while others have relegated it to an insignificant corner of the freshman course. This in turn has the effect of sending the student into the quantitative analysis course with little or no knowledge of the equilibrium principles and chemical facts on which quantitative methods are based, and of sending him into the physical chemistry course to learn why substances behave as they do without having any very accurate notions of how they behave. This is like building a house without a foundation. It would seem far better to discard the arbitrary schemes of analysis forthwith, and to try to develop a course which clearly illustrates the fundamental principles and the manner in which they are applied in developing and using analytical procedures.

A curious fact about the theoretical subject matter of the traditional course in qualitative analysis is that it differs from what is included in the quantitative analysis course only in its aims, but not in its substance. Equilibrium principles appear in qualitative analysis in connection with sulfide separations (whose kinetic complications are usually conveniently ignored), and again in quantitative analysis in connection with gravimetric procedures and titration curves. Chemical arithmetic is also an important part of each course, and so are techniques of separation; the list could be extended almost indefinitely. This division makes it difficult to present a coherent view of the field, suggests a distinction between its two branches which is wholly false to fact, and obscures the similarities between only slightly different applications of identical concepts.

Dissatisfaction with the traditional course in quantitative analysis has been hardly less pronounced. The chief difficulty here seems to arise from the laboratory work that is assigned. There is no doubt that many—perhaps even most—students are so repelled by what they encounter in the quantitative analysis laboratory that they abandon whatever ideas they may have had of choosing analytical chemistry as a career. No other laboratory course in the curriculum is so nearly completely devoted to techniques instead of principles. For the sake of illustrating a variety of analytical reagents and manipulations, and for convenience in grading, the student is confronted with an assortment of artificial and unrealistic samples, and his life becomes a torment under the repeatedly applied lash of "filter, wash, ignite, and weigh." It is little wonder that this dulls his senses and leads him to regard analytical chemistry as the province of technicians with cookbooks.

Analytical Principles: Basis for Integration

From such considerations it appeared to us that the optimum organization of an introductory course in analytical chemistry would involve the complete integration of qualitative and quantitative applications of the basic principles involved, and would employ the laboratory time available to illustrate these principles themselves rather than their eventual practical application in the hands of the analyst. In this spirit it seemed difficult to find any substantial justification for the traditional exclusion of organic chemistry from the introductory analytical course. Too often the undergraduate curriculum fosters the notion that organic chemistry and analytical chemistry have little or nothing in common—a notion which is very far from the truth. There is no reason why the sophomore who has had only a cursory previous acquaintance with organic chemistry cannot be given some idea of the place of organic reagents in inorganic analysis, the types of problems that are encountered in the elementary and functional-group analysis of organic samples, and other similar matters that lie on the borderline between the two fields.

Although it is more and more generally conceded that instrumental methods have a place in the introductory analytical course, there is little general agreement about the methods that should be included and the aims that are served by including them. One reasonable approach is that the total exclusion of such techniques gives a distorted view of the nature of modern analytical practice, but that the only techniques deserving more than the briefest of passing mentions in a sophomore course are those which bear an intimate and unmistakable relationship to the chemical principles at hand. Visual colorimetry is, of course, involved in such matters as the sensitivity of a qualitative test and the error in detecting the color change of an indica-

[1] Noyes, A. A., and Bray, W. C., "A System of Qualitative Analysis for the Rare Elements," The Macmillan Company, New York, 1927.

tor; from this to spectrophotometry is a very short step and one which is readily appreciated by the student, who gains from it in understanding as well as knowledge. Volumetric redox methods could hardly be discussed at all without introducing electrode potentials and redox titration curves, and to omit potentiometric methods altogether in this context, or to relegate them to another part of the course, would amount to sacrificing a valuable opportunity to clarify the essential theory. There are a few other similar techniques that merit inclusion, at least in the lecture material. However, many others occasionally found in quantitative analysis textbooks do not seem to conform to these criteria. Polarography is an example. No doubt this is a valuable and widely used technique of practical analysis, and no doubt its theory is closely related to that of a potentiometric titration. But few if any sophomores would be likely to find that a discussion of polarography cast much light on the nature of redox titrations. Of course it must be pointed out that our thinking on this question reflects the fact that advanced analytical courses are available to us for the presentation of these techniques. Where the sophomore course in analytical chemistry is the terminal undergraduate course in the field, the temptation to include a larger number of instrumental methods might be much more difficult to resist.

The first semester of this course is devoted to chemical equilibria, methods of detection and identification, and methods of separation, in that order. Some of the experiments assigned in the laboratory (where the chemists spend 9 hours per week, and all other students spend 6) deal with the equilibrium constant of the arsenic(III)–iodine reaction and the rate at which equilibrium is attained, the solubility product of strontium chromate and the solubility of this substance in various salt solutions, the dissociation constant of an acid-base indicator and its use in colorimetric *p*H measurements, the effect of *p*H on the solubility of calcium oxalate, the sensitivities of the tests for copper (II) carried out with several common selective reagents, the extent of coprecipitation of nickel(II) with hydrous ferric oxide under various conditions, the influences of various experimental conditions on the extraction of lead dithizonate into chloroform, and a number of other chemical phenomena of broad analytical importance. Visual colorimetry is employed extensively in these experiments because of its ease and rapidity, and because it serves to concentrate the students' attention on the principles being studied rather than on the tools and techniques employed. However, permanganimetric titrations are used in studying the solubility of calcium oxalate, and alkalimetric titrations are used to investigate the composition of the iron(III) precipitate obtained from a basic benzoate precipitation. Near the end of the semester the student is given the problem of devising a method of separating the possible constituents of a simple ionic mixture and estimating their concentrations; this involves a short search of the literature, the design and testing of a simple method of separation, the observation of some characteristic reactions of the assigned substances, and the selection of one that can be used to detect and estimate the concentration of each ion that may be present, and the combination of all of these into an analytical procedure which is then applied to an unknown. Not only does this constitute a real challenge, which the routine execution of a ready-made procedure does not, but it also gives the student a fairly accurate idea of the kind of thinking that is involved in practical qualitative analysis and in the design of analytical procedures.

The lectures during this first semester follow much the same order as the laboratory, and consume 2 hours per week for all students. Following a rather detailed treatment of chemical equilibria in solutions, the general principles of coordination chemistry are described and related to such topics as selective and specific reagents, chelons and other complexing agents, and stepwise complex formation. The phenomenon of salt effect is introduced quite early and is employed wherever practicable during the remainder of the course. Stoichiometry appears about midway through the semester and is handled by using the mole as the fundamental unit throughout; this reflects our belief that the use of the equivalent carries no practical advantage, but only the possibility of much confusion and misunderstanding. Methods of separation, including precipitation, extraction, ion exchange, and other chromatographic processes are then discussed.

The second semester is begun with a brief treatment of systematic descriptive inorganic chemistry, in which the periodicity of the chemical properties of the elements is emphasized as far as this is realistic. It then continues with such matters as titration curve theory; the techniques, reagents, and procedures employed in volumetric and gravimetric analysis and in the instrumental procedures mentioned above; and outlines the general considerations involved in organic analysis.

The laboratory work during this term represents an extension and further development of the experiments performed in the first semester. Additional techniques of separation, including ion-exchange and paper chromatography, are examined. Aging processes and coprecipitation in crystalline precipitates are demonstrated by analysis. The remaining experiments are carried out using the more exact techniques commonly associated with quantitative analysis. They include several experiments devoted to common unit operations, such as weighing and gravimetric and volumetric determinations of water and chloride. The latter half of the term is designed to illustrate the manner in which an analytical procedure is developed and tested. The conditions appropriate to the iodometric determination of copper in pure solutions are first examined in some detail. Thus, the effects of varying *p*H, iodide concentration, order of addition of reagents, and other procedural details are studied quantitatively by analyzing known solutions. A similar study of the behavior of another element, such as antimony, provides information which the student can use to devise a quantitative method for the determination of copper in the presence of this other element. After testing the performance of his method with mixtures of known composition, he is given an unknown mixture to analyze. The term closes with an analogous series of experiments dealing with a similar problem in organic functional group analysis.

A textbook embodying this approach to the introductory course in analytical chemistry is in preparation

and will be published by the McGraw-Hill Book Company.

The philosophy and structure of our second-semester junior-year course have been described in detail elsewhere,[2] and need not be repeated here. Suffice it to say that the principal emphases are on the relations among the various instrumental techniques described—on the interconnections of their theoretical foundations and on the reasons that cause one to be preferred to another for an attack on any particular problem of research or analysis—and that the laboratory work consists of applying these techniques to a single simple research problem insofar as this is possible. Thus the student is enabled and encouraged to compare the kinds of information that can be obtained by the different techniques. This is much more difficult to do if the techniques are employed in analyzing different samples or if they are applied to different research problems. Experience dating back to 1950 has convinced us that no other approach yet proposed gives the student so accurate a picture of the similarities and differences among the various techniques or of the ways in which they are applied to a problem in analytical chemistry.

Undergraduate Thesis Work in Analytical Chemistry

The thesis written during the senior year serves a number of purposes in the student's education. It gives him the opportunity to apply what he has learned in previous years to a real and challenging research problem, and provides him with a powerful stimulus to go on to graduate work and ultimately to a career in chemical research. Not only does it constitute an excellent introduction to what he will encounter in graduate school or in a research group in an industrial laboratory, but it also gives him the opportunity to confirm or reject his first choice of a field of specialization by showing him exactly what present-day research in that field consists of. His work in the laboratory introduces him at close range to the patterns of thought that constitute an experienced adviser's approach to a research problem and to the observations that are made during its course, and this gives him a better appreciation of the interaction among experiment, observation, and hypothesis than he could obtain in any other way. The actual writing of the thesis is, in most cases, his first real encounter with technical writing, and from it he can learn much about the necessity for concise and exact use of his native tongue. Quite incidentally, his performance during his thesis research provides his adviser with the material for a nearly perfectly exact prediction of the probable course of his career in this field during the succeeding few years.

It is expected that the research and writing connected with his thesis will consume about 15 hours per week of the student's time for the two semesters of his senior year. Therefore it is highly desirable to guide students toward projects which, while having a real significance that is visible to them at this stage of their development, are of sufficiently restricted scope to indicate that solutions to them can reasonably be expected in this length of time. Artificial or "make-work" problems would generally be recognized as such, and hence would fail to arouse interest; whereas to work for so long on a problem without achieving any worthwhile results is a rather severe blow to the student's morale. On the other hand, to know that the efforts of his predecessors have usually merited publication in the current literature and that his own problem will probably lead to the same goal if his work on it is assiduous and careful enough gives him an incomparable incentive to put forth his very best efforts. A few problems that have been selected during recent years are the polarographic determination of chlorate, the electrogeneration of chromous ion as a reagent for coulometric titrations, the separation of carrier-free strontium-89 from cesium-137, the determination of basicity constants of very weak bases, and intermetallic compound formation in mixed amalgams of zinc and cobalt.

Sometime during his junior year the student consults with several faculty members to find out their specific areas of research interest. It is our custom to describe two or three problems to each student at this point. The student is then entirely free to select an adviser and to choose one of the problems proposed to him. He is generally assigned a considerable amount of reading in the area of the problem of his choice, and this is usually done during the summer between his junior and senior years. During the actual conduct of his research and the writing of his thesis, he usually spends between a few minutes and a few hours each week with his adviser discussing the work he has done, the work that should be done next, and any other material in the general field of this research that his adviser brings up. Sometime during this year he addresses the regular divisional seminar in analytical chemistry, usually on a topic closely related to his research problem. At the end of the year, when the final draft of his thesis has been completed, he undergoes an oral examination administered by his adviser and one or two other members of the faculty, at least one of whom represents a field other than that in which he has worked. This examination is not confined to his thesis; it may range over the entire subject matter of his undergraduate curriculum. Not only does this guarantee that the student will not have uncomprehendingly carried out the directions of his adviser, but it also gives him an idea of what to expect on similar occasions in graduate school.

The caliber of this thesis program, and the extent to which it seems to confirm the students' interest in analytical chemistry, are indicated by the facts that, with rare exceptions, all of our bachelor's theses in analytical chemistry during the last few years have proved to be publishable in the current literature. Although the careers of some have been interrupted by military service, all of our recent thesis students have at least applied for admission to some graduate school with the intention of pursuing graduate study in the analytical field.

The final form of this over-all program has been in effect for too short a time to permit a full evaluation of its results. We are confident, however, that it provides a sound, comprehensive, well-integrated, and thoroughly modern treatment of this important part of the undergraduate student's training in chemistry.

[2] Meites, L., and Thomas, H. C., "Advanced Analytical Chemistry," McGraw-Hill Book Company, Inc., New York, 1958.

Henry Freiser
University of Arizona
Tucson

Integrating Analytical Chemistry in the Undergraduate Curriculum

The subject of analytical chemistry affords a magnificently logical opportunity to develop the unity of chemical science inasmuch as its philosophy, principles, and techniques provide the sturdy foundation of the many branches of chemistry.[1] Indeed, it might not be out of place to propose a redefinition or rather a reclassification of the divisions of chemistry into just these two: synthesis and analysis. This classification represents something more than a defensive response to the physical chemist's definition of his field as "everything that interests me." Chemists usually are concerned either with making new materials (inorganic or organic synthesis) or with the structure and composition of matter (analysis). Naturally, these activities are inspired and illuminated by theoretical principles which are or should be the concern of all chemists.

Any reasonable definition of analytical chemistry permits us to realize that even in the "traditional" undergraduate curriculum a thread of analytical chemistry runs through all the courses. At the University of Arizona we have attempted to realize more fully the significant advantages of such connections by extending the practice of analysis in both directions (i.e., both earlier and later than the second year) as well as by enriching the second-year course devoted primarily to analytical chemistry. The virtue, if any there be, lies more in recognition of current trends in analytical education than in initiating novel programs. Improvements that have been made reflect good taste more than originality. Our debt is to many leaders in chemical education, but I wish to acknowledge especially the inspiration afforded by Professor Ernest Swift who dared to expose freshmen to quantitative analysis[2] and to Professor Richard Ramette for his use of lively and meaningful experiments in the analytical chemistry laboratory.[3]

[1] Use of the word "integration" in the title of this paper needs clarification at the outset. This term has been applied to descriptions of curricula in which analytical chemistry has been assimilated into the rest of the program and has lost its identity as a separate course. I disavow this heresy which is obviously *dis*-integration rather than integration of analytical chemistry in the undergraduate curriculum.

[2] SWIFT, E. H., J. CHEM. EDUC., **35**, 248 (1958).

[3] RAMETTE, R. W., J. CHEM. EDUC., **33**, 610 (1956).

Presented as part of the Symposium on Educational Trends in Analytical Chemistry, sponsored jointly by the Divisions of Analytical Chemistry and Chemical Education, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

The Freshman Course

At the University of Arizona we have organized our freshman chemistry courses into two main offerings: one, in the main sequence, is required of all students who plan to take more than one year of chemistry, and the other is a terminal course. For the main sequence course, the three-hour laboratory has been liberated from the inexorable routine of one experiment each week. In laboratory sections of up to forty students, techniques of quantitative measurements such as use of the analytical balance and buret figure significantly in the first semester. Experiments such as solubility of a salt, determination of per cent composition, acid-base titration, extraction, and molecular weight determination are carried out on an individual basis to emphasize the adult nature of college students' introduction to chemical science and to prevent boredom on the part of those who have had good high school chemistry courses. We find students prefer this approach infinitely more than the cookbook. Students use a bound, blank laboratory notebook in place of the semi-assembled prefabricated crutches that pass for laboratory manuals designed apparently to further aggravate the galloping illiteracy prevalent on university campuses.

The laboratory work of the second semester continues along the same lines but is noteworthy for the inclusion of a generous sampling of semimicro qualitative analysis exercises as a frame of reference for the study of ionic equilibrium and the chemistry of the metals. It also takes advantage of the high interest in chemistry that qualitative analysis generates. Since I have spoken out against freshmen qualitative analysis courses in the past,[4] I should explain that my reversal is only apparent. What I was and still am opposed to is the *substitution* of a slim freshman qualitative course in place of a serious course in analytical separations. At Arizona, no such substitution has taken place; rather a taste of qualitative has been added to the freshman year foretelling of the pleasures ahead.

The Second-Year Course

By the end of the first year our students are, we hope, "lab broken" to the extent that there are those who have taken the traditional one-semester quantitative analysis course. In their second year, devoted entirely to analytical principles and techniques, the students are called upon to develop further their laboratory skills and apply these to experiments of interest in the theory and

[4] FREISER, H., J. CHEM. EDUC., **34**, 387 (1957).

practice of analysis. The first semester, Analytical Chemistry I, is devoted to principles and methods of determination; and the second, Analytical Chemistry II, is concerned with principles and methods of separations processes. In the more conventional sequence these concepts were developed in a qualitative analysis course along with the great multitude of associated chemical reactions. This great mass of material usually overwhelmed both instructor and student. The "reverse" order permits a development of the principles of analytical chemistry which is more logical and which is easier on both teacher and student. There is no appreciable increase in difficulty for the student who takes quantitative without qualitative analysis, but there is a significantly beneficial effect upon the level at which the second semester's offering can be taught.

The laboratory instruction in Analytical Chemistry I is imbued with the philosophy that a properly trained analyst is not merely an automaton for receiving samples and delivering results. What are the over-all aspects of the problem for which the analysis is being performed? What use will be made of the results? These are questions which not only make the analyst's job more interesting but are essential to the proper conduct of his analytical work. It is, of course, recognized that whereas almost all chemists do analytical work, relatively few students become professional analysts. Hence, a good number of the laboratory exercises represent applications of analytical techniques to solution of problems of more general analytical interest; for example, the estimation of molecular weight, or determination of rate and equilibrium constants. (See Table 1.) An attempt is made to include exercises in analysis of organic as well as inorganic substances. A selection of relatively simple problems in organic functional group analysis impresses the student with the general applicability of the techniques he is learning and probably has a salutary effect on his ability to grasp organic chemistry.

Inasmuch as the students have previously learned to manage a standard analytical balance, they have single pan automatic reading balances at their disposal (Mettler Model H-5).[5] These serve dual functions in improving student morale and in permitting a significant increase in the number of assigned determinations. Ten such balances are a comfortable number to accommodate almost two hundred students in groups of up to forty at one time.

The lecture portion of the course is devoted to intensive treatment of stoichiometry, statistical treatment of data, and various aspects of chemical equilibrium. (See Table 2.) These topics may be more comfortably developed in the quantitative analysis course in view of the relatively small number of chemical reactions dealt with in the laboratory.

The second semester's work, Analytical Chemistry II, is devoted to the development of the principles and

Table 1.

Analytical Chemistry I Laboratory Exercises

1. Use of the Mettler balance
2. a. Calibration of buret
   b. Determination of molecular weight by the Dumas method.
3. Determination of the degree of hydration of a salt
4. a. Preparation of standard silver nitrate solution
   b. Estimation of the atomic weight of barium
   c. Assay of an amine via its hydrochloride
5. a. Preparation and standardization of sodium hydroxide
   b. Comparison of NaOH with phenolphthalein and methyl orange
   c. Assay of aspirin
   d. Determination of the rate of ester hydrolysis
   e. Exchange capacity of a cation exchange resin
   f. *Assay of concentrated HCl. Use of hydrometers and micro ("lambda") pipets
6. a. Potentiometric acid-base titration (pH meter)
   b. Preparation of buffers
   c. Colorimetric determination of pH
   d. *Determination of the ionization constant of a weak acid or base
7. *Non-aqueous titrations of very weak acids and bases
8. a. Preparation and standardization of EDTA
   b. Determination of total water hardness. Statistical analysis of water hardness data
   c. Determination of calcium and magnesium in a limestone
   d. *Exchange equilibria for calcium on a cation exchange resin. Effect of citrate ion.
   e. *Solubility of calcium sulfate in solutions of varying sulfate concentrations
9. a. Preparation and standardization of $KMnO_4$ solution
   b. Preparation and standardization of $Ce_2(SO_4)_3$ solution
   c. Preparation and standardization of $K_2Cr_2O_7$ solution
   d. Comparison of the iron titer of a solution in which $SnCl_2$–$HgCl_2$ reduction is used
10. Potentiometric titration of an oxidation-reduction reaction
11. a. Standardization of iodine solution
    b. *Distribution of iodine between immiscible solvents
    c. *The tri-iodide equilibrium
    d. Vitamin C assay
    e. Estimation of copper
    f. *Assay of magnesium via bromate-bromide titration of the 8-quinolinol chelate
12. a. Gravimetric standardization of HCl
    b. Estimation of nickel with dimethylglyoxime
    c. Precipitation from homogeneous solution
13. a. The absorption spectrum of MnO_4^- (with a Bausch & Lomb "Spectronic 20")
    b. Colorimetric determination of manganese
    c. Colorimetric estimation of riboflavin
    d. Colorimetric determination of nickel with dimethylglyoxime

The unstarred experiments are to be done by all students. Those marked with an asterisk are optional.

Exercise 2 is included to develop technique of weighing liquids and vapors and an understanding of buoyancy corrections.

Exercises 5c, 8b, 9d, and e afford practical application of statistical treatment of data.

A number of exercises promote the feeling of unity in organic and inorganic analysis (2b, 4c, 5c, d, and 11d, 13c).

Table 2.

Analytical Chemistry I Lecture Outline

Scope and significance of analytical chemistry
Principles of stoichiometry
Statistical treatment of data
Application of chemical kinetics and chemical equilibrium to analytical problems
Solubility equilibria
pH—meaning, measurement, and calculation
Brønsted acid-base theory—non-aqueous titrations
Acid-base titration curves
Buffers
Lewis acid-base theory and metal ion buffers
Oxidation-reduction stoichiometry
Oxidation potentials
Gravimetry—properties of precipitates
Colorimetry and spectrophotometry

[5] See, for example, the discussion in the Chemical Instrumentation Series, THIS JOURNAL, **36**, A67 (1959).

techniques of analytical separations processes. The laboratory work focuses attention on inorganic separations particularly those involving the metal ions. In addition to exercises in precipitation as a means of separation, work in solvent extraction, ion exchange, paper chromatography, and volatilization is included using elements which range the periodic table. Considerable use is made of EDTA titrimetry and of colorimetry in estimation of metals after separation. Optional exercises include zone refining, fractional distillation, and gas chromatography using organic mixtures.

The classroom and lecture portion of Analytical Chemistry II is devoted to the exposition of the principles of separation processes in general and to the theory and practice of the separation processes employed in the laboratory. Considerable emphasis is placed on the subject of coordination compounds which is of such vital significance in understanding the chemistry of metals in solution.

The benefits of this analytical training accrue to the laboratories of both organic and physical chemistry. Functional group analysis may be continued naturally and easily in both semesters of the organic laboratory. The major benefit in the physical chemistry laboratory lies in using the time released by moving certain experiments to the analytical laboratory to develop a research atmosphere. In the physical chemistry laboratory, the integration of principles and techniques mastered in previous course work is directed toward the inclusion of laboratory projects which, but for the accident of prior publication, may be classified as research.

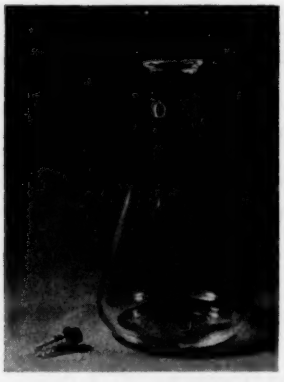
EDITOR'S NOTE

The remaining papers of the symposium will appear in the July issue of THIS JOURNAL. They set forth the status of analytical chemistry courses at MIT (D. N. Hume), Northwestern (R. C. Bowers and D. D. DeFord), Harvey Mudd (R. A. Whiteker), and Carleton (R. W. Ramette).

Removable Vacuum Connectors for Filter Flasks

W. R. Doty

California Research Corporation, Richmond, California



Almost all breakage of the common filter flask occurs at the point where the vacuum connection is sealed to the filter flask body. To reduce the breakage problem, we have developed a tooled glass tubulation, using a Neoprene rubber grommet[1] at the base. This is inserted into a drilled hole in the flask neck. The flexibility of the joint prevents breakage of the assembly in normal use. An additional advantage is that the tubulation and grommet can be removed and inserted into a clean flask. The rubber vacuum tubing need not be disconnected.

The design has been tested for several months in this laboratory and has received broad acceptance. The cost of the change is small. We estimate that the reduction in breakage is at least 80%.

[1] A mold for these grommets and the grommets themselves were fabricated by the Oliver Tire and Rubber Company, Oakland, Calif.

Acceleration of Flash Distillation

S. Kasman and **L. E. Rubin**

Polaroid Corporation, Cambridge 39, Mass.

Flash distillation is a common technique for concentrating a dilute solution of a nonvolatile solute. A distilling flask is heated on a steam bath, or by other suitable means, and subjected to the vacuum of an aspirator or vacuum pump to which it is connected through a trap, receiver, and efficient condenser. The solution is aspirated into the distilling flask from a reservoir or an addition funnel. We have found that the rate of distillation of solvent can be enhanced considerably by a trivial change in the above apparatus. A preheater condenser (Liebig, West, bulb, or coil) is mounted on the distilling flask and steam is passed through its jacket. The dilute solution is introduced to the distilling flask through the preheater condenser. By a suitable choice of preheater condenser and of the rate of flow of influent it is easily possible to concentrate the dilute solution to "dryness" in the condenser itself.

Using an ordinary four-bulb 24/20 standard taper condenser as the preheater and a steam heated three-neck 2-liter distilling flask fitted with a bubbler, we have concentrated alcohol solutions at the rate of six liters per hour for several hours running. A simple, highly effective, nonrestrictive spray trap was made from a one-neck, 24/40 500 ml flask by sealing a 24/40 male joint in the bottom.

Leallyn B. Clapp[1]
Brown University
Providence, Rhode Island
and **Corwin Hansch**
Pomona College
Claremont, California

Identification of Amino Acids in a Protein Hydrolysate by Paper Chromatography

The use of paper chromatography at the undergraduate level and for beginning biochemistry students (*1*) appears to be highly desirable because of its widespread use in chemical and biochemical research. The technique is so simple that it may seem a magical answer to laboratory questions rather than a tool for solving genuine problems unless a few catches in interpretation appear to puzzle the experimenter.

Identification of amino acids in a protein hydrolysate has all the reality of the puzzles that appear in chemical research, the spur to attain improvement by running "just one more" chromatogram, and the satisfactions of some positive results for the beginner.

The directions given below assume a preliminary discussion of chromatography by the instructor and preferably a class demonstration, for example (*2*), with a drop of ink on filter paper.

Solutions

Prepare 5% aqueous solutions of amino acids or their hydrochlorides (*a*).

One basic and two alternative acidic solvents are described. Basic solvent: A, 2 volumes of 2-propanol, 1 volume of 2% ammonium hydroxide. Acidic solvents: B, 2 volumes of 2-propanol, 1 volume of 2% acetic acid; C, 75 ml of 2-butanone, 25 ml of propionic acid, 30 ml of water (*4*). (This is the approximate volume needed for use in a 4-liter beaker as described below.)

(Solvents A and B ascend 20 cm in about 12 hr, solvent C in about 4 hr.)

The spray reagent is 0.1% solution of ninhydrin in 95% ethanol (*3*). The best development of colors obtains if 5 ml of collidine is added to 100 ml of the spray solution. An ordinary household De Vilbiss nasal sprayer may be used.

Paper

Cut large sheets (46 × 57 cm) of Whatman No. 1 or No. 3 paper to give four 23:× 28.5-cm sheets. Draw a light pencil mark 15 mm from the bottom of one sheet and mark 11 positions on the line 2.5 cm apart.

Chromatography of Amino Acids

Make one chromatogram using 11 known amino acids (*b*) from the table (*5*) with solvent C. Apply the amino acid solutions to the paper with capillary pipets (*3*), allow to dry, staple the paper in the form of a cylinder (*3*), place in solvent C in a 4-liter beaker (*c*), cover carefully with aluminum foil, and allow to ascend (*7*) 4–6 hr. Dry the paper, spray with ninhydrin solution, dry again, and then warm in an oven at 80–90° for three minutes to develop the colored spots (*d*). Determine the R_f values (*3*) for the 11 chosen amino acids.

After a judicious choice of groups of amino acids from the first chromatogram or the literature (*4*) apply solutions of all the amino acids in the table to be considered (*b*) to seven positions, on each of two sheets of paper as before. To the other four positions apply protein hydrolysate of *p*H 7 and *p*H 4, using double or triple amounts on one position (*e*).

Protein Hydrolysate

In a 200-ml round-bottomed flask, add 1 g of gelatin to 30 ml of 9 *N* sulfuric acid and reflux 6–18 hr (*f*). Add the hydrolysate to a slurry of 44 g of barium hydroxide (octahydrate) in 60 ml of water. Collect the barium sulfate on a large Büchner funnel and wash with 10 ml of water (*g*). Determine the approximate *p*H with an outside indicator and bring to *p*H 7 with 1 *N* sulfuric acid or sodium hydroxide (*h*). Bring a portion of the solution to *p*H 4.

Notes

(*a*) More dilute solutions (*3*) require longer waiting time for drying on the part of the student since larger volumes are needed.

(*b*) Tyrosine and phenylalanine are destroyed by the hydrolytic treatment (*6*) of the gelatin and may be omitted from the list the student receives. Methionine need not be considered since at most it appears in low percentage in gelatin. Histidine and hydroxylysine give weak colors with ninhydrin and have low sensitivity to the reagent and may also be omitted from consideration. Polypeptides do not give colors with ninhydrin, and lower peptides do not seem to interfere (*9*).

(*c*) Consistent R_f values are obtained only if the solvent has stood in the covered beaker some time previous to use.

(*d*) A ventilated hood will allow the paper to dry in about 15 minutes. If the oven is above 90°, beginners may easily scorch the paper. Longer development time at 80° is therefore preferable for students.

(*e*) In practice students get an idea of the variation in R_f values that may be expected from four trials on the same sheet. The safety factor in using double or triple amounts in some positions is desirable. R_f values are changed appreciably if the *p*H is much below 3 (*8*); long "tails" develop on some amino acids; and the spots tend to blur into each other, especially in solvent A.

[1] NSF Faculty Fellow at Harvey Mudd College, Claremont, California, 1959.

(*f*) Amino acids appear within 4 hours (*9*) and little advantage accrues for this experiment in refluxing beyond 8 hours. The reflux may be interrupted as often as necessary. Some amino acids may indeed be destroyed by the 18-hour period. The lysine and arginine spots were noticeably less dense.

(*g*) Alternatively 6 *N* hydrochloric acid may be used in the hydrolysis and most of the excess acid removed with lead oxide.

(*h*) In case acid is added, barium sulfate may easily be removed this time by gravity filtration.

Results

The choice of gelatin as the protein appears to be a happy one since two of the amino acids derived from it give distinctly different colors with the reagent ninhydrin from all the other amino acids; proline (yellow) and hydroxyproline (orange). These are present in rather high percentages and so are easily detected even though the colors do not contrast so sharply with white paper as the blue to purple shades produced by other amino acids.

The positions of 5 amino acids are clear in all three solvents: leucine, valine, proline, alanine, and hydroxyproline. Although the R_f values of the last three are close together in all three solvents, the blue crescent of alanine (in A and B) seems always to be pushing a yellow ball of proline ahead of it and trailing a small brown spot of hydroxyproline (orange spot alone). In solvent C the first four amino acids give distinct spots but the brown spot of hyroxyproline is inside the larger glutamic acid red-violet one.

In solvent A two heavy spots appear below these five, the first a composite of glycine, serine, and threonine (histidine also if not all destroyed in the hydrolysis) closely followed by a second of glutamic acid, aspartic acid, arginine, and lysine.

In solvent B the same acids appear in two spots but the order is different: the first contains glutamic acid and threonine and the lower spot glycine, serine, aspartic acid, lysine, and arginine.

The order of appearance of the amino acids in solvent C is that expected of the published R_f values (*4*). In the protein hydrolysate the four top spots are followed by the fifth of hydroxyproline inside the large glutamic acid spot. The spot next lower than the one containing glutamic acid and hydroxyproline is a composite of aspartic acid, glycine, and threonine with a serine tail. A light blue dumbbell follows in the lowest position containing arginine and lysine in that order.

A chromatogram made with a strip of paper (46 cm) suspended from a wire over a liter graduate containing solvent C gave nine distinguishable spots from the protein hydrolysate: leucine, valine, proline, alanine, glutamic acid, hydroxyproline, aspartic acid-glycine-threonine-serine, arginine, and lysine. Solvents A and B gave no appreciable improvement in separations in the long strip over the 20-cm distance. Clayton and Strong (*4*) report identification of 12 amino acids (a prepared mixture) by using solvent C in a two-dimensional chromatogram.

The experiment described can be made of varying difficulty. By asking only for the identification of five amino acids, the beginner can be assured of success. By giving the student known R_f values for amino acids and omitting the ones that will not appear in the protein hydrolysate the time can be shortened and the experiment limited to making two chromatograms. An experiment of senior research level could be made by using the present experiment as a starting point and then turning to the identification of amino acids in other protein hydrolysates. The student should realize he is near the frontier of research in this field: a complete separation of amino acids in bovine serum albumin, for example, by paper chromatography is comparatively recent (*10*).

Acknowledgment

One of us (L. B. C.) is grateful to Harvey Mudd College for use of their laboratory facilities during the tenure of an NSF Faculty Fellowship. Valuable talks with Professor Freeman C. Bovard, Claremont Men's College, facilitated the work appreciably.

Composition of Amino Acids in Bovine Collagen (*5*) (as g residue/100 g)

Alanine	7.6	Leucines (3)	4.8
Arginine	7.9	Lysine	4.0
Aspartic acid	5.5	Methionine	0.7
Glutamic acid	10.0	Phenylalanine	3.7
Glycine	19.9	Proline	12.7
Histidine	0.7	Serine	2.7
Hydroxylysine	1.1	Threonine	2.0
Hydroxyproline	12.1	Tyrosine	1.3
		Valine	2.9
			99.6

Literature Cited

(1) Patton, A. R., J. Chem. Educ., **27**, 60 (1950).
(2) Hazel, J. F., "A Basic Laboratory Course in College Chemistry," 2nd ed., John Wiley & Sons, Inc., New York, **1957**, p. 194.
(3) Slaten, L., Willard, M., and Green, A. A. Sr., J. Chem. Educ., **33**, 140 (1956).
(4) Clayton, R. A., and Strong, F. M., *Anal. Chem.*, **26**, 1362 (1954).
(5) Bowes, J. H., and Kenten, R. H., *Biochem. J.*, 43, 358 (1948).
(6) Martin, A. J. P., and Synge, R. L. M., *Adv. in Protein Chem.*, **2**, 1 (1945).
(7) Williams, R. J., and Kirby, H., *Science*, **107**, 481 (1948).
(8) Lederer, E., and Lederer, M., "Chromatography," Elsevier Publ. Co., New York, **1954**, p. 197.
(9) Partridge, S. M., and Davis, H. F., *Nature*, **165**, 62 (1950).
(10) Redfield, R. R., and Barron, E. S. G., *Arch. Biochem. Biophys.*, **35**, 443 (1952).

GUEST AUTHOR
H. Goldwhite
Manchester College
of Science and Technology
Manchester, England

Textbook Errors, 25

The Side-Chain Halogenation of n-Alkyl Benzenes

A number of textbooks[1] state that in the halogenation of the side-chains of normal alkyl benzenes with elemental halogens there is a strong tendency for halogenation to take place preferentially at the carbon atom next to the aromatic nucleus. Indeed some books imply that halogenation occurs exclusively in this position in the side-chain. However when the literature on this type of reaction is examined it does not bear out this conclusion. In fact past workers have found in general that the reaction leads to mixtures of isomers from which it is hard to isolate pure compounds.

There is very little recent work on side-chain halogenation, and much of the early work gave results which were hard to interpret; the following conclusions are those best supported by original work.

Chlorination

Ethylbenzene. The chlorination of boiling ethylbenzene gave mainly β-phenylethylchloride (*1*, *2*). By contrast the chlorination of ethylbenzene in the cold, with illumination of the reaction mixture, gave the isomeric α-phenylethylchloride (*3*). A more recent investigation of the chlorination of boiling ethylbenzene in diffused daylight showed that a mixture of the α- and β-chlorides was produced plus some α-, β-dichloride, $C_6H_5CHClCH_2Cl$ (*4*). The authors of this article suggested that an increase in light intensity gave an increased amount of α-phenylethylchloride, but their experiments were not precise enough to establish this point. They also suggested that the complexity of their reaction mixture arose from subsequent reactions of β-phenylethylchloride which was first formed. This could lose hydrogen chloride to form styrene which could then combine either with the hydrogen chloride, to give α-phenylethylchloride, or with chlorine, to give the α-, β-dichloride.

n-Propylbenzene. A careful investigation (*5*, *6*) showed that the main product of chlorination of boiling *n*-propylbenzene was the β-chloride, $C_6H_5CH_2CHClCH_3$.

Bromination

Ethylbenzene. The bromination of ethylbenzene in sunlight at 0° gave first α-phenylethylbromide and then α,α-dibromoethylbenzene, $C_6H_5CBr_2CH_3$, with no evidence of the formation of any β-bromo derivatives (*7*). The bromination of boiling ethylbenzene—in complete contrast to its chlorination—gave a mixture of α-phenylethylbromide and the α-, β-dibromide, $C_6H_5CHBrCH_2Br$, identical with the product of the addition of bromine to styrene (*8*, *9*).

n-Propylbenzene. The bromination of this compound followed the pattern shown by ethylbenzene. Bromination in the cold and in sunlight gave first the α-bromide and then the α,α-dibromide, $C_6H_5CBr_2CH_2CH_3$ (*10*). Bromination at 160°C gave a dibromide which was probably $C_6H_5CHBrCHBrCH_3$ (*11*).

Are Predictions Justified?

These experiments show that the ordinary halogenation—and especially chlorination—of these alkylated benzenes does not favor the α-position of the side-chain over the β-position. It is interesting to speculate about why the assertion that the α-position is favored has crept into textbooks. The reasoning behind the assertion may have run as follows: the halogenation is certainly a radical reaction, and of all the side-chain radicals which could be produced by the abstraction of hydrogen the α-radical ($PhCHCH_3$ as it would be from ethylbenzene) is likely to be the most stable; in consequence the halogenation will most probably yield α-halo derivatives.

The results show that this is an insufficient argument. The interesting experiments recently carried out on the competitive chlorination and bromination of mixtures of toluene and cyclohexane (*12*) show that it is necessary to take into account many factors besides radical stabilization in discussing halogenation. The argument outlined above would lead to the conclusion that toluene (giving a stabilized benzyl radical) would be halogenated more rapidly than cyclohexane, and, in fact, in the competitive bromination toluene reacted about 60 times as fast as cyclohexane. But in competitive chlorination cyclohexane reacted 11 times as rapidly as toluene. This is interpreted as meaning that in the transition state of the chlorination of toluene the methyl C—H bond is not completely broken and that, in consequence, the stabilization of the incipient benzyl radical contributes very little toward making the rupture of the bond easy.

The conclusion to be drawn from this is that without

Suggestions of material suitable for this column, and guest columns suitable for publication directly are eagerly solicited. They should be sent with as many details as possible, and particularly with references to modern textbooks, to Karol J. Mysels, Department of Chemistry, University of Southern California, Los Angeles 7, California.

[1] Since the purpose of this column is to prevent the spread and continuation of errors and not the evaluation of individual texts, the source of errors discussed will not be cited. To be presented the error must occur in at least two independent standard books.

many more experimental results, and without a more detailed knowledge of the mechanism of these radical reactions, it is unwise to predict what the products of any given halogenation will be.

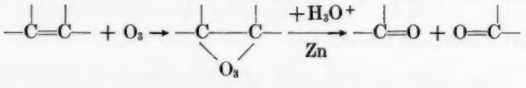
Literature Cited

(1) Fittig, R., and Kiesow, J., *Ann.*, **156**, 245–51 (1870).
(2) Anschütz, R., *Ann.*, **235**, 329f (1886).
(3) Schramm, J., *Monatsh.*, **8**, 102 (1887).
(4) Evans, E. B., Mabbott, E. E., and Turner, E. E., *J. Chem. Soc.*, **1927**, 1163.
(5) Errera, G., *Gazz. chim. ital.*, **14**, 504 (1884).
(6) *Ibid.*, **16**, 310–25 (1886).
(7) Schramm, J., *Ber.*, **18**, 350–5(1885).
(8) Radziszewski, Br., *Ber.*, **6**, 492–4 (1873).
(9) *Ibid.*, **7**, 140–3 (1874).
(10) Schramm, J., *Ber.*, **18**, 1274f (1885).
(11) Radziszewski, B., *Compt. rend.*, **78**, 1153f (1874).
(12) Russell, G. A., and Brown, H. C., *J. Am. Chem. Soc.*, **77**, 4578–82 (1955).

Jacob G. Sharefkin
and **Aaron Ribner**
Brooklyn College
Brooklyn 10, New York

The Qualitative Detection of Olefins by Ozonolysis

The addition of ozone to the carbon to carbon double bond and reductive hydrolysis of the ozonide to two carbonyl moieties, which is known as the Harries (*1*) reaction, is the most reliable method for locating the site of an olefin bond (*2*). More recently,



Boer and Kooyman (*3*) have employed ozonolysis as a titrometric procedure for the quantitative estimation of olefin unsaturation. However, the cost of commercial ozonizers and the difficulties in constructing laboratory models has prevented their use in undergraduate laboratory courses in organic chemistry despite the fact that this important reaction is invariably included in the curricula and texts of such courses.

The oxidation level of the carbonyl places it at the "center of the universe" of organic functional groups for it may be obtained by oxidizing primary and secondary alcohols, reducing acid derivatives, hydrolyzing geminal dihalogen compounds, and hydrating acetylenes as well as oxidation of olefins and many other reactions. These relationships and transformations become more valuable in teaching functional groups because the carbonyl compounds are readily characterized and identified as 2,4-dinitrophenylhydrazones (*4*, *5*).

Among the factors contributing to the scarcity of ozonolysis experiments in the undergraduate organic laboratory are the cost of available commercial equipment and the glass blowing and electrical equipment needed for laboratory models like that of Smith (*6*) and those listed by Bailey (*7*). The apparatus described below was assembled for less than $10.00 and provides elementary organic chemistry students at Brooklyn College with a qualitative test for the olefin bond that requires less than five minutes.

Presented before the Division of Chemical Education at the 136th Meeting of the American Chemical Society, Atlantic City, September, 1959.

Construction of the Capacitor

The body of the ozonizer is a high voltage air capacitor consisting of alternate aluminum plates that are spaced 1-cm apart and are enclosed in a glass box that has inlet and outlet tubes on two opposite faces. At first, four of the eight aluminum plates, which are all 10-cm square, are held against a 10- × 14-cm Bakelite base and two $^1/_8$-in. holes are drilled in the adjoining corners along the 10-cm edge. The remaining four

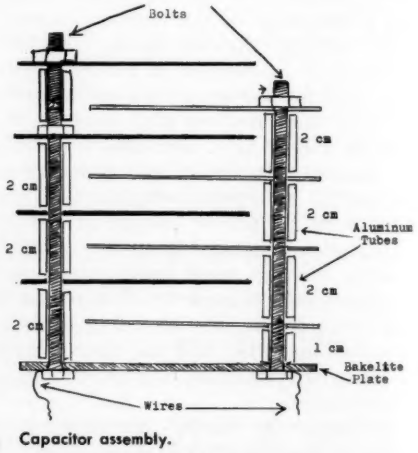


Figure 1. Capacitor assembly.

aluminum plates are now placed against the Bakelite base and two $^1/_8$-in. holes are drilled in the remaining two corners of the base as well as these plates.

To assemble the plates, first slip four $^1/_8$-in. iron bolts that are 10 cm long through the four holes in the base and then place over two adjacent iron bolts two aluminum tubing separators that have a $^1/_8$-in. i.d. and are 1 cm long before inserting these bolts through the two holes of one aluminum plate. Now two aluminum tubing separators that are 2 cm long are slipped over the other two iron bolts which now receive the

second aluminum plate. The process is repeated with two 2-cm aluminum separators on the first two bolts and this alternation continued until the eight plates are in place, four on each side, and these are then held firmly with a washer and a nut on each bolt as shown in Figure 1. A heavily insulated wire is now connected to each set of plates.

The glass enclosure for the capacitor is made from two 12- × 12-cm and four 12- × 14-cm panes of window glass. These six glass sides are fitted together with four 14-cm long and eight 12-cm long pieces of right angle aluminum stripping whose ends are cut at 45° angles to meet in the corners. The four 14-cm right angle aluminum strips are cemented with glazier's putty, or any cement that will make an air-tight joint, to the four glass plates along their 14-cm edges to make a hollow rectangle into which the capacitor is inserted. A notch is made on the edge of each of the two remaining glass plates and four 12-cm right angle strips are cemented to the four edges of each. A 6-mm hole is bored through the aluminum stripping of each plate where the glass is notched and a 10-cm long piece of glass tubing is inserted and cemented in place. These two end plates are cemented to the ends of the hollow rectangle containing the capacitor, and the glass enclosure is tested for air tightness.

Operation of Ozonizer

The source of the high voltage is a model A Ford induction coil which receives its current from a toy electric train transformer that is plugged into the 110-v line. However, any induction coil may be used if there is a vibrator in the circuit and a drop of glycerine is placed on the vibrator points when the spark becomes weak after operating for some time. Care must be taken to avoid grounding the capacitor by mounting it on either asbestos or rubber. Either air or oxygen enters the inlet tube which is near the Bakelite plate and the ozonized gas passes from the exit tube into two side arm test tubes connected in series.

To determine the percentage yield of ozone twelve liters of air are siphoned through the ozonizer in one hour with the apparatus shown in Figure 2 and the ozonized air bubbled through a neutral 5% KI solution in the side arm test tubes. Calculations based on the titration of the liberated iodine with standard thiosulfate indicated the formation of 0.8 to 1.25 per cent of ozone per mole of oxygen in the air.

Detection of Olefins

The qualitative characterization of olefins is effected by a modification of the procedure of Bonner (*8*) for the preparation of derivatives in which olefin ozonolysis is carried out in an alcoholic acid solution of 2,4-dinitrophenylhydrazone and the hydrazone is formed *in situ*. Two drops or 0.1 g of olefin are dissolved in 2.5 ml of 0.05 *M* 2,4-dinitrophenylhydrazine which is 2 *M* with respect to HCl in methanol as solvent. Ozonized air is passed through this solution and the sign of reaction is a deep red color that develops when 1 drop of the reaction mixture is pipetted into 2 ml of 2 *M* KOH in methanol.

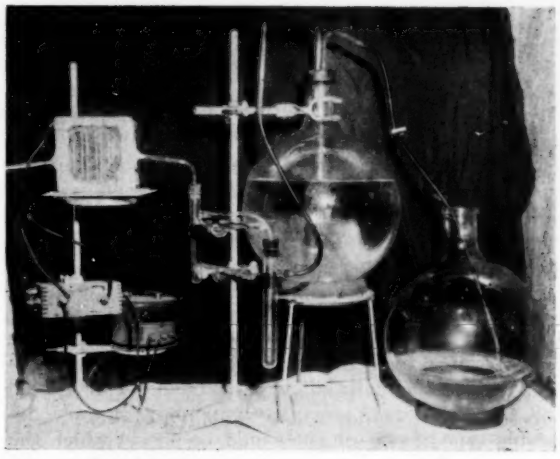


Figure 2. Ozonizer assembly.

A blank test should be performed on the olefin prior to ozonolysis, for many alkenes react with the oxygen of the air to form peroxides that give a positive test with the dinitrophenylhydrazine reagent; the olefin should then be distilled over sodium until the blank test is negative. Positive tests with 2-pentene, 1-octene, styrene, benzene, and *m*-xylene were obtained in 2 min. while indene required 1 min. and camphene, 4 min.

Literature Cited

(1) Harries, C., *Ber.*, **36,** 1933 (1903).
(2) Gilman, H., "Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, **1943,** Vol. I, p. 636.
(3) Boer, H., and Kooyman, E. C., *Anal. Chim. Acta*, **5,** 550 (1951).
(4) Davidson, D., and Perlman, D., "A Guide to Qualitative Organic Analysis," 2nd ed., Brooklyn College Press, Brooklyn, N. Y., **1958,** p. 49.
(5) Cheronis, N. D., and Entriken, J. B., "Semimicro Qualitative Organic Analysis," 2nd ed., Interscience Publishers, Inc., New York, **1959,** pp. 264, 390.
(6) Smith, L. I., Greenwood, F. L., and Hurdlik, O., "Organic Syntheses," Collective Vol. III, John Wiley & Sons, New York, **1955,** p. 673.
(7) Bailey, Philip S., *Chem. Rev.*, **58,** 985 (1958).
(8) Bonner, W. A., J. Chem. Educ., **30,** 452 (1953).

Tested Demonstrations—Big Fourth Edition

The new edition (163 pages plus index) contains all of the Alyea Demonstration Abstracts, the original set of 24 Alyea Tested Demonstrations, and 72 of the current Chem Ed Tested Demonstrations. This book is the biggest bargain in chemical education. See page A298 of May, 1960.

Robert E. Buckles
and **Donald F. Knaack**
State University of Iowa
Iowa City

Styrene Iodochloride:

A proof-of-structure experiment

Among the experiments which have been designed for courses in beginning organic chemistry, very few actually allow the student to determine the structure of an organic compound. A very desirable type of experiment would be one in which the structure of a reaction product is elucidated by the student from a consideration of: (1) the original reaction of synthesis, (2) the results of a series of qualitative tests on the product, and (3) the results of a degradation of the product to a known compound which could be identified. Most experiments of this type are far too involved for classes in first-year organic chemistry. We recommend the proof of structure of styrene iodochloride as an experiment of this type for courses in beginning organic chemistry. On the basis of trials with more than 200 students we believe that the preparation of this compound and the determination of its structure are well within the capacity of the average student in first-year organic chemistry.

The Structure of Styrene Iodochloride

Styrene iodochloride is the product resulting from the addition of the elements of iodine monochloride to styrene. Two possible addition products must be considered as shown in equations (1) and (2).

$$C_6H_5CH{=}CH_2 + ICl \rightarrow C_6H_5CHCl{-}CH_2I \quad (1)$$

$$C_6H_5CH{=}CH_2 + ICl \rightarrow C_6H_5CHI{-}CH_2Cl \quad (2)$$

If the product is 1-chloro-2-iodo-1-phenylethane as formed by the reaction of equation (1), dehydrohalogenation could give either α-chlorostyrene as in equation (3) or β-iodostyrene as in equation (4).

$$C_6H_5CHCl{-}CH_2I + OH^- \rightarrow C_6H_5CCl{=}CH_2 + I^- + H_2O \quad (3)$$

$$C_6H_5CHCl{-}CH_2I + OH^- \rightarrow C_6H_5CH{=}CHI + Cl^- + H_2O \quad (4)$$

On the other hand if the product is 2-chloro-1-iodo-1-phenylethane as formed by the reaction of equation (2), dehydrohalogenation could give either β-chlorostyrene as in equation (5) or α-iodostyrene as in equation (6).

$$C_6H_5CHI{-}CH_2Cl + OH^- \rightarrow C_6H_5CH{=}CHCl + I^- + H_2O \quad (5)$$

$$C_6H_5CHI{-}CH_2Cl + OH^- \rightarrow C_6H_5CI{=}CH_2 + Cl^- + H_2O \quad (6)$$

If either of the α-halostyrenes is hydrated the product would be acetophenone as in equation (7) while either of the β-halostyrenes would give phenylacetaldehyde as in equation (8).

$$C_6H_5CX{=}CH_2 + 2H_2O \rightarrow C_6H_5COCH_3 + H_3O^+ + X^- \quad (7)$$

$$C_6H_5CH{=}CHX + 2H_2O \rightarrow C_6H_5CH_2CHO + H_3O^+ + X^- \quad (8)$$

The final carbonyl product can be identified as its phenylhydrazone. The positions of the chlorine atom and of the iodine atom can be deduced from this identification and the identification of the halide ions formed in the dehydrohalogenation step and in the hydration step.

The characterization and structure of styrene iodochloride, which have been reported in the chemical literature, are somewhat obscure. The reaction of styrene with iodine in the presence of mercury (II) chloride has been reported (*1*) to give an iodochloride of mp 40.6° while the reaction of styrene with Wijs solution (iodine monochloride in glacial acetic acid) has been reported (*2*) to give an iodochloride of mp 46°. In each case the product was assumed to be 1-chloro-2-iodo-1-phenylethane, but the positions of the iodine atom and the chlorine atom in the molecule were not actually established. In another case the product of the reaction of styrene with iodine monochloride in dilute hydrochloric acid was not isolated, but analyses of reaction mixtures by quantitative hydrolyses were interpreted as indicating the addition product was at least 95% 1-chloro-2-iodo-1-phenylethane (*3*). The assumption that the iodochloride was 1-chloro-2-iodo-1-phenylethane in these cases was based on the observations that the chlorine atom was preferentially removed either by silver ion (*2*) or by solvent molecules capable of solvating ionic intermediates (*1*, *3*). This interpretation is based on the consideration that the formation of a carbonium ion intermediate[1] in these reactions takes place at the secondary benzyl carbon atom in preference to the primary carbon atom as illustrated in equations (9) and (10).

$$C_6H_5CHClCH_2I + Ag^+ \rightarrow C_6H_5{}^+CHCH_2I + AgCl \quad (9)$$

$$C_6H_5CHClCH_2I \overset{\text{solvent}}{\rightleftharpoons} C_6H_5{}^+CHCH_2I + Cl^- \quad (10)$$

The carbonium ion intermediate would then react with a solvent molecule or with an available anion to give a stable product. On the basis of modern theories of organic chemistry, the preferential removal of chloride ion when a carbonium ion intermediate is formed, is strong evidence for the iodochloride being 1-chloro-2-iodo-1-phenylethane. Also if Markovnikov's rule is obeyed as it is for the addition of bromine chloride (*4*) or of hypobromous acid (*5*) to styrene the iodochloride would be expected to have this structure. These results do not constitute a complete proof of structure, however.

In preliminary experiments which led to the design of the experiment for beginning students in organic chemistry we found the iodochloride of styrene had mp 40.5–41.0° which is consistent with the value of 40.6° which has been reported (*1*), but not with the value of 46° which has also been reported (*2*). We

[1] Reactions of this type which form carbonium ions by the removal of an anion are usually classified as S_N1-type reactions.

also established the identity of the iodochloride as 1-chloro-2-iodo-1-phenylethane by means of the reactions (*4*, *6*) outlined in equations (1), (3), and (7). Thus, Markovnikov's rule was followed on the basis of iodine monochloride adding as positive iodine and negative chlorine as shown in equation (11).

$$C_6H_5CH{=}CH_2 + ICl \rightarrow C_6H_5{}^{+}CHCH_2I + Cl^{-} \rightarrow C_6H_5CHClCH_2I \quad (11)$$

The Student Experiment

The reaction series was developed on a small scale for use as a student experiment. The conditions for the dehydrohalogenation and the hydration were established by a series of experiments in which the crude products were assayed by gas chromatography. The procedure was then tested by several groups of students as part of their laboratory work during the second semester of first-year organic chemistry.

The small scale addition of iodine monochloride to styrene was found to be a very satisfactory reaction for a laboratory experiment. The main problem encountered by the student was caused by the excess of iodine present in most samples of iodine monochloride. Some of this iodine added to styrene to form the diiodide and was often not removed completely by the reducing agent used to remove excess halogen even though the addition reaction was reversible. During the isolation of the iodochloride the diiodide reverted to iodine and styrene giving a red violet color to the product which should have been white. Too much iodine impurity in the product made the structure proof less satisfactory.

In spite of the fact that the iodochloride is a low melting solid no difficulty was encountered in obtaining it crystalline even when it was extensively colored with iodine. The students consistently obtained yields varying from 70–90% of product of mp around 37°. Recrystallization of the product was not necessary if it was not colored too darkly. Crude α-chlorostyrene was obtained by the students in yields varying from 30–40% by the dehydrohalogenation of the iodochloride. This crude product was shown by gas chromatography to be contaminated consistently with styrene (from the diiodide) but never with phenylacetylene. The crude α-chlorostyrene was hydrated at room temperature in 80% sulfuric acid for five days. After this time the crude acetophenone was obtained by the students in yields varying from 20–50%. It was shown to contain no styrene nor α-chlorostyrene after this time by means of gas chromatography. A phenylhydrazone was easily prepared from this crude ketone. If too much iodine was present in the original iodochloride and if too much liquid was steam distilled during the isolation of the acetophenone, impure iodoform (mp 114–15°) was sometimes obtained as a by-product. Its presence made isolation of the phenylhydrazone difficult. The iodoform was presumably formed as a by-product during the dehydrohalogenation reaction when iodine was present in the basic solution. This by-product would have been extracted with the α-chlorostyrene and would have distilled during a prolonged steam distillation of the acetophenone produced in the hydration reaction.

The experiment has been designed so that the student isolates the iodochloride, takes its melting point, and carries out qualitative tests on the product for halogen. A sodium fusion followed by tests for halide ion and for iodide ion is carried out (*7*). A test with sodium iodide in acetone for vicinal dihalides is also used (*8*). The student next carries out the dehydrohalogenation of the iodochloride and identifies the hydrogen halide eliminated as hydrogen iodide by qualitative tests. He carries out the hydration of the α-chlorostyrene and identifies the hydrogen halide formed as hydrogen chloride. The carbonyl compound formed is identified as acetophenone from the melting point of its phenylhydrazone (105°) compared with that of the phenylhydrazone of phenylacetaldehyde (58°). From these observations and the assumption that the carbon skeleton of styrene is not changed by the addition reaction with iodine monochloride, the student can deduce the structure of the iodochloride as outlined in equations (1), (3), and (7).

The series of experiments can be completed comfortably by the average student in three laboratory periods of approximately two and one-half hours each. Between the second and third periods at least five days should elapse so that the hydration reaction mixture can remain at room temperature for that long.

Preliminary Experiments

Iodine Monochloride Solution. A 5% solution of iodine monochloride[2] (50 g) in carbon tetrachloride (950 g, 596 ml) was made up for use in the addition experiments. Its keeping quality was checked iodometrically. It was found that when it was well-stoppered it lost strength at the rate of less than 1% per month. A solution which was six months old was found to work well in the addition experiment.

1-Chloro-2-iodo-1-phenylethane. To 200 ml (320 g) of 5% iodine monochloride (0.098 mole) in carbon tetrachloride was added to 10 ml (9.0 g, 0.096 mole) of styrene. The product was isolated as described in the Student Procedure to yield 25.7 g (100%) of crude 1-chloro-2-iodo-1-phenylethane of mp 37–9°. A small amount was rapidly crystallized several times from 95% ethyl alcohol to yield a product which had a maximum mp 40.5–41.0°.

Anal. Calc'd. for C_8H_8ClI: C, 36.1; H, 3.03. Found: C, 35.9; H, 3.03.

α-Chlorostyrene. To a solution of 21 ml of 6 *N* aqueous sodium hydroxide in 52 ml of methanol was added 26.0 g (0.096 mole) of 1-chloro-2-iodo-1-phenylethane. The mixture was heated to boiling and allowed to cool slowly to room temperature. Addition of 500 ml of water caused the separation of an oil which was removed and dried over anhydrous potassium carbonate. Distillation yielded 8.8 g (66%) of α-chlorostyrene, bp 80–2° (20 mm).

Acetophenone. To a cooled solution of 16 ml of concentrated sulfuric acid in 6 ml of distilled water was added 7.0 g (0.05 mole) of α-chlorostyrene. The mixture was allowed to stand for five days with occasional shaking. Dilution with water caused the separation of an oil which was extracted with benzene. The benzene solution was dried over anhydrous calcium

[2] Iodine monochloride is available commercially, or it may be synthesized by the reaction of gaseous chlorine with solid iodine (*9*).

sulfate and distilled to yield 4.1 g (69%) of acetophenone, bp 88–90° (22 mm). A solution of 0.5 ml of this acetophenone in 2 ml of isopropyl alcohol was treated with water one drop at a time until the solution was almost turbid. A drop of glacial acetic acid and 0.2 ml of phenylhydrazine were added and the solution was warmed gently. Cooling yielded the phenylhydrazone which was crystallized from isopropyl alcohol to give a sample of mp 103–4°.

Styrene Diiodide. A solution of 0.5 g of iodine in 5 ml of styrene was reddish-brown. When cooled in dry ice this solution became lighter in color and deposited crystals which appeared to be nearly white. Further cooling froze the entire mixture. As it warmed up the styrene melted and the light-colored crystals were still present. The crystals appeared reddish-tan on the filter paper when the solution was filtered rapidly. On standing for a few minutes they started to darken and after several hours only a red-brown oil was present. The solution of iodine in styrene became more violet when dissolved in carbon tetrachloride. This carbon tetrachloride solution was decolorized when shaken with dilute aqueous sodium thiosulfate. On standing the carbon tetrachloride solution became pink. Heating accentuated the effect giving a violet solution which became pink as it cooled.

Gas Chromatography. The presence of products and by-products in the carbon tetrachloride solutions obtained from the small scale experiments on dehydrohalogenation and hydration was detected by gas chromatography. Measurements were made with a Perkin-Elmer Model 154 Vapor Fractometer. Two-meter columns were used. Helium was used as a carrier gas. The pressure was 25 psig and the flow rate was 0.76 ml per sec. The data obtained for products and possible products at 150° are summarized in Table 1. Even though the elution times for styrene and for phenylacetylene were nearly the same for the column filled with silicone oil on Celite (Column C) it was possible with this column to show that the by-product in the crude α-chlorostyrene was styrene. A separate peak appeared for phenylacetylene when it was added to the crude α-chlorostyrene.

Table 1. Summary of Elution Times in Experiments with Gas Chromatography at 150°

Compound	Elution time, min. Column A (Didecyl phthalate on celite)	Column C (Silicone oil on celite)
Iodine monochloride	..	2.2
Styrene	6.6	2.8
Phenylacetylene	6.6	2.6
β-Chlorostyrene	19.3	5.8
Acetophenone	24.8	6.1

It was possible to detect any α-chlorostyrene in the crude acetophenone only when the didecyl phthalate column was used (Column A). With the C column the two peaks overlapped badly. When a carbon tetrachloride solution of the pure addition product 2-chloro-1-iodo-1-phenylethane was used on the C column at 150°, small amounts of styrene and iodine monochloride were detected and no other peaks were observed. At 225° the same general result was obtained except that the styrene peak was much larger and the iodine monochloride peak was obscured by the extensive solvent peak.

Student Procedure

Addition of Iodine Monochloride to Styrene. Measure 2.0 ml (1.8 g) of styrene into a 125 ml Erlenmeyer flask. Slowly mix into the flask 40 ml (63.9 g) of a 5% solution of iodine monochloride (50 g in 596 ml) in carbon tetrachloride.[3] After several minutes the solution will become violet. Shake the carbon tetrachloride solution with a dilute aqueous solution of a reducing agent such as sodium bisulfite, sodium sulfite, or sodium thiosulfate. The violet color should disappear. If it does not, add more of the aqueous reducing agent and shake the mixture again. After several minutes the violet color will begin to reappear in the carbon tetrachloride layer. Shake the solution again to discharge the color. Repeat this operation over a period of 15 or 20 min. Separate the layers. Wash the carbon tetrachloride layer with 50 ml of water. Pour the carbon tetrachloride layer into a 50-ml distilling flask. Attach a water-cooled condenser and a thermometer to the distilling flask. Distill as much carbon tetrachloride as possible from the solution as it is heated on a steam bath. If the residue shows a violet, iodine color, wash it into a separatory funnel with 10 ml of carbon tetrachloride and repeat the washing with aqueous reducing agent followed by a water wash and distillation.

Disconnect the condenser and attach the side arm of the distilling flask to an aspirator by means of a rubber tube. Replace the thermometer with a glass tube reaching into the bulb of the distilling flask. Adjust the aspirator so that it draws air through the apparatus fairly rapidly as the distilling flask is heated on the steam bath. After about 20 min pour the residue into a small beaker. Stir the oil until it is crystalline. Determine the melting point and the weight of the solid product.

Obtain a dry 3-in. soft glass test tube. Place a piece of sodium metal the size of a small pea in the test tube. Heat the test tube in a small flame until the bottom is dull red. Remove the test tube from the flame and add a small piece of the styrene iodochloride the size of a drop of liquid. Repeat the heating, add another small sample of the iodochloride, and heat again to dull redness. Allow the test tube to cool and break it with a pestle in a mortar containing 3 ml of isopropyl alcohol. When the reaction of the sodium with the alcohol is completed, add 20 ml of distilled water. Boil the solution for a few minutes and filter it. Acidify the resulting solution with dilute nitric acid and test a portion of it for halide ion with silver nitrate solution. Test another portion of the acidified solution for iodide ion with a drop of 5.25% sodium hypochlorite solution (commercial laundry bleach) in the presence of a few drops of carbon tetrachloride to dissolve any iodine which is formed. The presence of iodine is observed as a violet color in the carbon tetrachloride layer.

Dissolve a small piece (about the size of a drop of liquid) of the styrene iodochloride in the minimum volume of acetone. Add this solution to 1 ml of sodium iodide in acetone[4] and observe the result.

Dehydrohalogenation. Weigh the iodochloride into a flask. Add 2 ml of methanol per gram of iodochloride. Connect a reflux condenser to the flask and heat it on a steam bath until the iodochloride has dissolved. Carefully pour 6 *N* sodium hydroxide (0.8 ml per gram of iodochloride) down the condenser. Heat the mixture to boiling and then allow it to cool. Pour the reaction mixture into a separatory funnel and rinse the flask with 25 ml of distilled water which is also poured into the separatory funnel. Extract the aqueous solution with two 5-ml portions of carbon tetrachloride and separate the layers. Test the aqueous layer for halide ion and for iodide ion as described for the solution from the sodium fusion of the iodochloride. Wash the carbon tetrachloride layer with 25 ml of water. Separate the layers and discard the water. Distill the carbon tetrachloride layer on a steam

[3] Avoid breathing either iodine monochloride vapors or carbon tetrachloride vapors. If iodine monochloride solution is spilled on the skin, treat as for a bromine burn with glycerol.

[4] The stock solution is prepared from 15 g of sodium iodide and 100 ml of acetone. The solution is usually lemon yellow. It should be stored in a brown bottle. The solution should be discarded if it becomes red-brown (*8*).

bath until no more solvent comes over. Use the residue in the next step immediately.

Hydration. Add 2.8 ml of concentrated sulfuric acid carefully to 1.0 ml of distilled water. When this diluted acid has cooled mix it carefully with the residual product of the dehydrohalogenation and pour the mixture into a small glass-stoppered bottle or flask. Shake the container several times and then allow it to stand for at least five days. At the end of this reaction time neutralize the reaction mixture exactly to a light pink color with dilute sodium hydroxide solution in the presence of a drop of phenolphthalein indicator solution. Steam distill this neutralized solution until about 50 ml of water has distilled. Test the residual aqueous solution in the distilling flask for halide ion and for iodide ion as described earlier. Extract the aqueous distillate with two 5-ml portions of carbon tetrachloride. Distill the carbon tetrachloride solution from a steam bath. Dissolve the residue in 2 ml of isopropyl alcohol. Add water drop-wise until the solution is nearly turbid. Add 0.2 ml of phenylhydrazine[5] and one drop of glacial acetic acid. Gently warm the reaction mixture for a few minutes. Cool the solution with stirring to induce crystallization. Determine the melting point of the phenylhydrazone as soon as it is obtained. It decomposes on standing. If the product is impure, crystallize it from a small amount of isopropyl alcohol before the determination of the melting point.

[5] Care should be taken with phenylhydrazine. It is a skin poison. If spilled on the skin wash with dilute acetic acid and then water.

From the observations made during this experiment and the fact that the phenylhydrazone of phenylacetaldehyde has mp 58° and that of acetophenone has mp 105°, give the formula showing the identity of the iodochloride of styrene.

Literature Cited

(1) Winstein, S., and Grunwald, E., *J. Am. Chem. Soc.*, **70**, 828 (1948).
(2) Ingle, H., *J. Soc. Chem. Ind.*, **21**, 587 (1902).
(3) Ingold, C. K., and Smith, H. G., *J. Chem. Soc.*, **1931**, 2742.
(4) Buckles, R. E., and Long, J. W., *J. Am. Chem. Soc.*, **73**, 998 (1951).
(5) Buckles, R. E., and Maurer, J. E., *J. Org. Chem.*, **18**, 1585 (1953).
(6) Emerson, W. S., and Agnew, E. P., *J. Am. Chem. Soc.*, **67**, 518 (1945).
(7) Shriner, R. L., Fuson, R. C., and Curtin, D. Y., "The Systematic Identification of Organic Compounds," 4th ed., John Wiley & Sons, Inc., New York, **1956**, pp. 57–61.
(8) Shriner, R. L., Fuson, R. C., and Curtin, D. Y., "The Systematic Identification of Organic Compounds," 4th ed., John Wiley & Sons, Inc., New York, **1956**, p. 158.
(9) Cornog, J., and Karges, R. A., *Inorg. Syntheses*, **1**, 115 (1939); Sandin, R. B., Drake, W. V., and Leger, F., *Org. Syntheses*, **II**, 197 (1943).

V. Alexander Gordieyeff* and **Ethel B. Hackley**
U. S. Army Chemical Warfare Laboratories
Army Chemical Center, Maryland

A Micromethod for Measuring Interfacial Tension

In 1920, A. Ferguson and P. E. Dowson described an ingenious modification of the capillary tube method for the measurement of surface tension.[1] This modification eliminated the difficult task of preparing capillary tubes of a truly uniform diameter; instead of measuring the rise of a liquid in a capillary,[2] the liquid may be forced back to the lower end of the tube immersed in the liquid; the surface tension of the liquid is measured, using a convenient manometer, as a function of the pressure required to maintain this condition. The experimental setup is reproduced in Figure 1. The containers, F′, F″, filled with water, oil, or mercury, supply the pressure head required to keep the capillary tube free of liquid at equilibrium (lower diagram, Fig. 1). The pressure is read off a manometer, M, as the level difference, h. The pressure is varied by moving the lifting jack, J′, under the first container. The capillary tube is very slightly immersed in the test liquid by raising the thermostated container B, on a

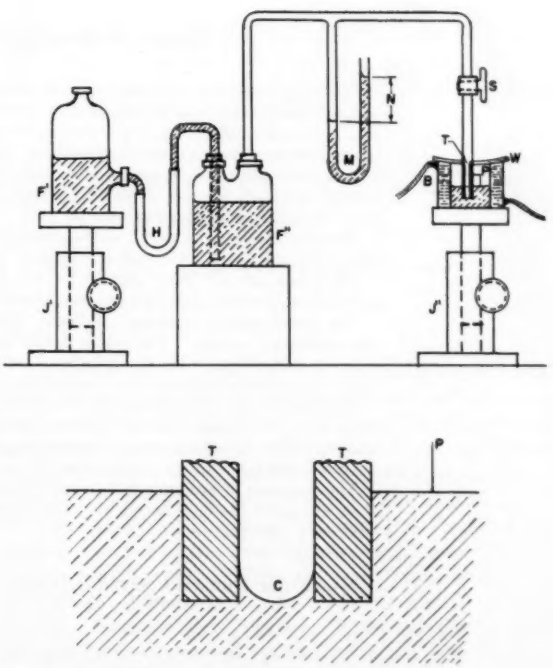


Figure 1. Apparatus for measuring interfacial tension.

* Deceased.

[1] Ferguson, A., and Dowson, E., *Trans. Faraday Soc.*, 16–17, 384–391 (1920–2).

[2] Partington, J. R., "An Advanced Treatise on Physical Chemistry," Longmans, Green and Co., Inc., London, **1951**, pp. 175–82.

lift jack, J″, until the contact is made with a fine pointer, P, attached to the capillary tube, T. The equilibrium position of the air-liquid interface is represented by the meniscus, C (lower diagram, Fig. 1). The distance between the pointer, P, the interface meniscus, C, and the manometer difference, h, are measured by a cathetometer. The orifice diameter of the capillary tube is determined under a microscope. The surface tension of the liquid is calculated according to the equation developed by Ferguson and Dowson as

$$T = g\frac{r}{2}(dh - d_1h_1) + g\frac{d_1r^2}{6}$$

The symbols denote: r = radius of capillary, h_1 = distance from the pointer, P_1, = to the end of the capillary (i.e., the depth of immersion), h = pressure head in manometer, d = density of experimental liquid, d_1 = density of liquid in manometer, and g = acceleration of gravity. The precision of the apparatus depends on the lifting mechanism for the pressure producing liquid (F′) and the sensitivity of the manometer, M. The latter may be greatly improved by using an inclined manometer. The apparatus, and for all practical purposes, the equation may be used without any modifications to measure interfacial tension of two immiscible liquids. The capillary, T, is brought in contact with a small volume of the test liquid and the back pressure so adjusted as to fill a few millimeters of the capillary bore while preventing air from entering the tube. The capillary end is drained of any excess of the test liquid and lowered into the container, B, filled with the other liquid. The pressure is adjusted until the meniscus equilibrium is obtained and the measurement carried out in the manner described by Ferguson and Davis for the air-liquid interfaces.

While the accuracy and precision of this method are generally somewhat inferior to those of other procedures, the speed of measurement, simplicity of apparatus and its operation, and the small volume of test liquids required for measurement seem to justify its use in many instances (See table).

The method was found useful for radioactive or highly toxic fluids and liquids available in micro and ultramicroquantities. Since the average capillary bore measures 0.1 to 0.5-mm in diameter, as little as 0.25 mm^3 may be required for an accurate measurement.

Table 1. Values of Interfacial Tension Between Immiscible Liquids Determined by the Reported Method and Recorded in the Literature, (t = 20°C)

System	Determined value dynes/cm	Recorded value, dynes/cm
Benzene–Water	34.96 ± 0.08**	35.00
Benzene–Mercury*	357.80 ± 0.60	357.20
Ethyl Oleate–Water	21.39 ± 0.07	21.34
n-Hexane–Water	51.15 ± 0.10	51.10
n-Hexane–Mercury	374.0 ± 0.75	375.0
Oleic Acid–Water	15.64 ± 0.05	15.59
o-Xylene–Water	36.00 ± 0.08	36.06

* Mercury used also as the manometer liquid instead of oil.
** Deviation range calculated on the basis of a 2–6 error.

Kinetic Molecular Theory from a Jukebox

When the authors first heard "The Witch Doctor's Song" blaring from the Student Center they were somewhat impressed with the intricacy of the lyrics which seemed to be something like, "Ooh, eeh, ooh ah ah, ting, tang, wallah wallah bing bang," with additions and variations. But more impressive was the way the student body learned the complicated syllables almost effortlessly. The idea of using music as a common basis of communication presented itself, and although perhaps open to criticism because of the effect on professorial dignity, the method may be defensible from the standpoint of pedagogical results.

The three states of matter and the associated motions of the physical species are described to the class in terms of the following analogies:

The gaseous state. Rock and Roll. Jazz. Wild gyrations, rapid random movement. Violent action of molecules with great spaces between molecular centers.

The liquid state. Waltzes, Ballads. Dreamy swing music. Plenty of movement but of a more subdued nature. The whole dance floor constantly changing pattern but much less space between molecules. Characterized by fluidity of the group and ability to accommodate to either large ballrooms or intimate cozy nooks, but always in motion!

The solid state. Foot patters. Observers. Chaperons who pick out a comfortable spot and relax for the evening, tapping their feet gently. Movement, but around a much more restricted vicinity, and both observers and chaperons packed very closely together in a crowded observation area, leaving the open spaces for the dancers.

The response of students in general chemistry, physical science, and general physics classes to these analogies has been excellent. Easy recall serves as a basis for satisfactory extension to more advanced concepts.

W. K. Easley and Glenn F. Powers

Northeast Louisiana State College
Monroe

George K. Estok
Texas Technological College
Lubbock

Temperature Change Demonstration with Selsyns

Lecture demonstration of temperature changes before large classes requires the use of apparatus that will make the changes visible on a large scale. Among previously described devices are a gas thermometer[1] and a thermocouple-actuated servomechanism.[2] Neither is as well suited to very large classes as is the presently described apparatus although they are more precise in operation. This apparatus is primarily designed to demonstrate qualitative temperature effects.

The essential features, as indicated in Figure 1, consist of a spirally-wound bimetallic temperature sensing unit *A* and a pair of inexpensive selsyns[3] (self-synchronous motors) designed for 110 v a.c. operation.

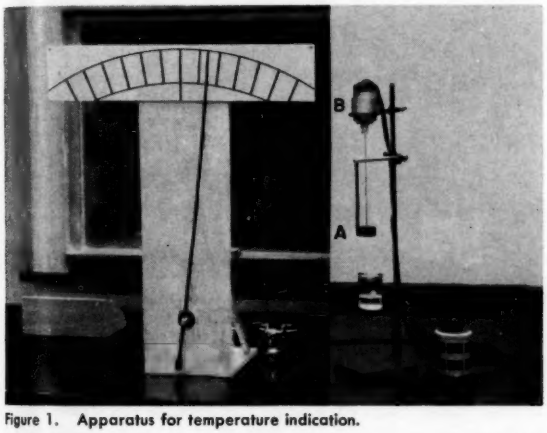


Figure 1. Apparatus for temperature indication.

The torque from the bimetallic spiral *A*, produced by a temperature change, is passed through a thin rod to a transmitting selsyn *B* which is connected electrically by a five-wire cable to a similar receiving selsyn at any convenient distance. Figure 2 indicates the parallel wiring required. The rotor of the receiver is fitted with a long light-weight, counter-balanced pointer which sweeps a graduated scale. The set-up may be portable, as shown, or permanently mounted on a wall.

The unit *A* in this case consists of a bimetallic strip one in. high and 37 in. long wound in a spiral and having an angular deflection of about 2.25° per 1°C and more than sufficient torque to turn the selsyn rotor.[4] The scale in Figure 1 is calibrated at 2°C per division.

A typical lecture demonstration of heats and cooling of solvation, and heat of reaction, might use the following (in 400-ml beakers, at room temperature): three beakers (B-1-a, -b, -c) each containing 150 ml of water; one beaker (B-2) with 100 ml of 1.5 *N* sodium hydroxide, and one beaker (B-3) with 100 ml of 1.5 *N* HCl.

With the selsyns in operation, B-1-a is raised to the thermal unit *A*, and the pointer is adjusted to the center of the scale remotely by loosening the coupling between selsyn *B* and the drive rod, and turning the rotor by hand. The coupling is again secured. B-1-a is lowered, 15 g of anhydrous calcium chloride added and dissolved as quickly as possible with stirring, and the beaker raised again. The pointer will move to the right, indicating a heating of about 10–11°. B-1-b is similarly manipulated, with the addition of 10 ml of concentrated sulfuric acid, and the pointer advances to the right about 10–12°. The use of B-1-c with 25 g of ammonium chloride causes a pointer movement to the left, showing a cooling of about 9°. To indicate a heat of reaction (neutralization), B-2 is raised and the pointer position noted. The contents of B-3 are then added to B-2 with swirling; the heat gives a change of 8–9° on the scale.

Although primarily designed for qualitative effects, the apparatus could be used for rough quantitative measurements if a correction were applied for the rather large heat capacity of the sensing unit, its support, and the beaker.

The bimetallic unit *A* is readily attacked by active agents, such as acids, and must be protected by some type of inert coating. In this case, the element and part of the mounting frame were coated with several dippings of thinned Tygon paint.

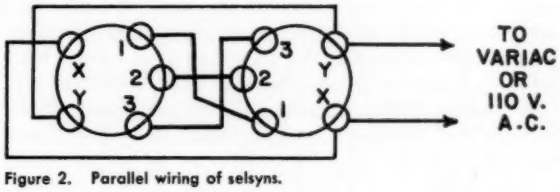


Figure 2. Parallel wiring of selsyns.

A word of caution is justified in connection with operation of the selsyns. If the two rotors are not synchronized when the full 110 v is first applied, there may be a violent agitation or turning of the rotors which may lead to damage. This may be obviated by making sure that the rotors are in proper orientation before application of power. This may be assured by marking the proper position of the sending rotor with respect to its encasing shell, while the pointer on the other rotor is located at center scale. Or, as is shown, a variable voltage transformer (Variac) may be used. Low voltage is first applied until the rotors synchronize; then full voltage may be applied.

[1] Wendlandt, W. W., and Estok, G. K., *School Science and Math.*, **LV**, 739–40 (1955).

[2] Dutton, F. B., J. Chem. Educ., **32**, 478–80 (1955).

[3] Selsyns of various voltages, sizes, and torques are available at nominal cost as government surplus items.

[4] The bimetallic unit was kindly furnished by the W. M. Chace Co., 1600 Beard Ave., Detroit 9, Mich.

J. K. Clinkscales, Jr.[1]
and Herschel Frye
College of the Pacific
Stockton 4, California

Building a High-Frequency Titrator for Instructional Use

Modern teaching of analytical chemistry must necessarily include more and more material involving instrumental methods of analysis. Most colleges and universities offer courses in instrumental analysis—often a one-semester or a one-quarter course—for which the investment in analytical instrumentation is considerable. Usually, the instruments so used may also be used for research in the larger institution, but the small college with limited opportunity for research on the graduate or advanced undergraduate level may have difficulty in justifying the outlay of several thousand dollars for one brief course. Fortunately, a number of useful instruments can be homemade for a few dollars—often from surplus parts; "dead stop" titrators and gas chromatographs are examples. The actual construction of such instruments may be made a part of an electronics or techniques course further enhancing the educational potential. With these ideas and the inherent limitations in mind, the authors undertook the construction of a high-frequency titrator.

A high-frequency titrator was chosen for construction primarily because of the uniqueness of the apparatus in that no direct contact is made between the measuring instrument and the solution being examined or analyzed. The 120 megacycle range was chosen in order that titrations could be run in the concentration range of 0.01 to 0.1 N according to the concentration curve of Blaedel and Malmstadt (*1*). Our experience with instruments of higher frequency indicates lack of stability above 120 megacycles.

Interest in high frequency titration methods began in 1946 with the work of Jensen and Parrack (*2*), and since that time applications of the method have been made to a wide variety of systems including titrations in non-aqueous media, the following of reaction kinetics, and binary solution analysis. The literature contains many articles describing these techniques. E. H. Sargent and Company has published an excellent bibliography (*3*).

The Apparatus

The instrument described in this paper is of the heterodyne type. Figure 1 represents the schematic diagram for the instrument exclusive of the power source; this latter may either be built up or purchased in kit form as indicated below. There are two separate oscillators mechanically shielded from each other and electrically isolated by the two identical buffer stages. The working oscillator (CS) has its frequency determined by the solution placed in the titrating vessel. The reference oscillator, however, is controlled by two condensers in parallel (C_{16} and C_{17}); this gives a relatively large tuning range and enables the operator to find the frequency of the working oscillator with rapidity and ease. As the two oscillators approach the same frequency, a heterodyne or beat frequency is detectable by earphone; this becomes zero beat when the two oscillators are tuned to exactly the same frequency. The buffers are R-C circuits designed to isolate the oscillators from each other. The mixer, detector, and audio stages are of standard design. Earphones were chosen because of ease of use and low cost. Figure 2 is a photograph of the instrument.

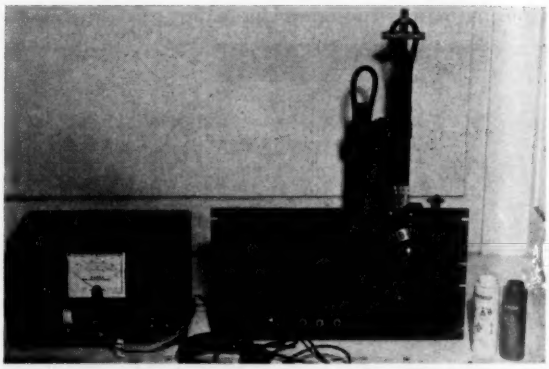


Figure 2. High-frequency titrator.

Construction of the unit is relatively simple and would make an excellent electronics project. The authors chose aluminum rather than cadmium-plated steel for the chassis to simplify construction of the unit. In design, the titrimeter is similar to that of West, Burkhalter, and Broussard (*4*), although the Clapp type oscillator has been replaced with 120 megacycle half wave oscillators. Choice of the 120 megacycle range is not unique; Johnson and Timnick (*5*) have constructed an instrument involving a single 120 megacycle oscillator and followed reactions by measuring grid current with a Sargent XXI polarograph. The authors feel that the instrument described in this paper is a stable, easily-operated titrimeter useful for instructional purposes.

The success of the instrument depends on several factors. Both oscillators have a common plate and filament supply, and any shift in frequency due to power supply fluctuation will cause the same shift in both oscillators. This is important because the difference between the oscillators is being measured at all times, and if a shift takes place, the difference is a constant. The use of a miniature 955 tube and a length of RG8 U flexible coaxial cable results in a very simple and stable oscillator arrangement at this frequency. For mechan-

[1] Present address: College of San Mateo, San Mateo, California.

ical stability, the RG8/U cables are supported on rigid wood frames attached to the chassis with bolts. All leads are kept short and mechanically stable; number 12 tinned copper wire is used in both oscillators. The 955 tube sockets are ceramic to minimize loss at high frequency and are mounted on rubber grommets to reduce vibration. The length of RG8/U coaxial cable is 90 cm for the working oscillator and several centimeters shorter for the reference oscillator; the additional capacitance of parallel condensers (C_{16} and C_{17}) compensates for this difference and keeps the tuning range near 120 megacycles. Shorter lengths of RG8/U cable were tried in an effort to achieve higher frequencies, but the resulting instruments were very unstable. The working oscillator is enclosed in a 2 × 3 × 6 in. box underneath the chassis. The reference oscillator has two tuning condensers in parallel; C_{16} is a 50 micromicrofarad split-stator; C_{17} is a 1–3 micro-microfarad butterfly. A knob on the side of the reference oscillator housing controls the large condenser; the small condenser is controlled from the front of the instrument by means of a National precision dial with a 1000:1 ratio.

The two oscillators have their plate voltages stabilized by an OA2 tube; the output of both oscillators is coupled through very small ceramic condensers (C_{18} and C_{23}) and coaxial cables to the grids of the buffer stages (V_6 and V_8). Each of these 6SK7 tubes is a low gain *R-C* coupled stage to isolate the oscillators from each other and to prevent pulling as the oscillators approach the same frequency. The output of both buffers feeds into a 6L7 mixer (V_7) where the two frequencies heterodyne. An addition signal and a difference signal are present, but only the difference signal is in the audio range; it is passed on to the 6H6 detector (V_3) for rectification. This small audio signal is then amplified through the two 6SJ7 pentode amplifiers (V_1 and V_2); the output is fed into the earphones. Each 6SJ7 grid has a separate gain control. In our instrument, the first control is located on top of the chassis and is operated by means of a screwdriver for optimum performance without overdriving the tube. The second gain control is located on the front panel and is adjusted as needed. The parts list gives the components used in the construction of the instrument.

The titration component is similar to one used by Johnson and Timnick (*5*). This unit is attached to the chassis by means of three silver-plated banana plugs. The solution vessel is made by cutting the top from a 2- × 6-in. plastic catsup bottle of the type readily available in most variety stores. This vessel is firmly held in place by means of fixed plastic rings and is mechanically stable although easily removable for cleaning. The oscillator electrodes are $^3/_4$- by 2-in. strips of silver curved slightly to fit around the plastic cup. This curvature complicates the theoretical treatment but is operationally adequate. Located above the electrodes is a ground ring made by drilling a $2^1/_{16}$-in. hole in a piece of aluminum 4 in. square and $^1/_2$-in. thick. This ground ring is important in preventing frequency shifts caused by the addition of liquid. Each experiment is begun with one hundred milliliters of liquid—

Parts List

Condensers (600 v., unless specified)

C_1, C_2, C_7, C_9, C_{11}	0.1 mfd
C_3, C_{10}	25 mfd (25v.)
C_4, C_5, C_6	10 mfd (450v.)
C_8	500 mmf mica
C_{12}, C_{13}, C_{14}, C_{15}, C_{24}, C_{25}, C_{26}, C_{27}	100 mmf mica
C_{16}	50–50 mmf (split-stator)
C_{17}	1–3 mmf (butterfly)
C_{18}, C_{23}	5 mmf mica
C_{19}, C_{22}	0.01 mfd
C_{20}, C_{21}	0.002 mfd

Tubes

V_1, V_2	6SJ7	V_5, V_9	955
V_3	6H6	V_6, V_8	6SK7
V_4, V_{10}	OA2	V_7	6L7

Coils

L_1, L_4	10 turns no. 22 wire around R_{15}
L_2, L_3, L_5, L_6	2.5 mh
L_7, L_8	90 cm length RG8/U coaxial cable

Resistors (1 watt unless specified)

R_1	4700	R_{13}	5K (10W)	R_{20}, R_{27}, R_{35}, R_{36}	250K	R_{29}	400
R_2, R_{12}	100K	R_{14}	4700, (2W)	R_{21}	600K	R_{30}	15K
R_3, R_7, R_8, R_{10}, R_{11}, R_{22}	500K	R_{15}	100, (2W)	R_{23}	680	R_{31}	100, (2W)
R_4, R_9	600	R_{16}, R_{17}	15K	R_{24}	330	R_{32}	1K
R_5	2K, (5W)	R_{18}, R_{28}	750K	R_{25}	150K	R_{33}	15K
R_6	2K, (5W)	R_{19}	400	R_{26}	5600	R_{34}	5K, (10W)

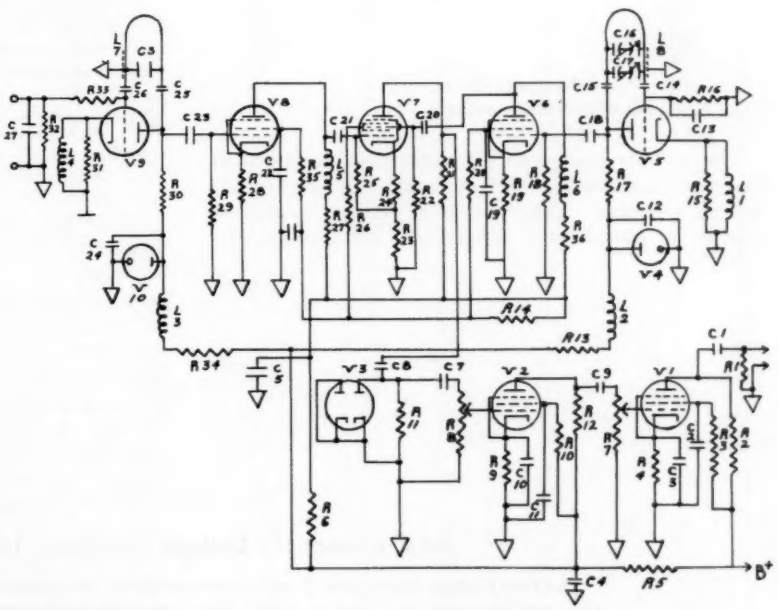


Figure 1. Circuit diagram.

enough to fill the plastic cup to a level above the ground ring. The authors have tried several other cell designs and find the above to be adequate for most work and preferable in some cases because of its flexibility and low cost.

The power supply is of conventional design. It should be constructed of quality components that are slightly overrated for cool efficient operation. The authors have used both their own power supply and one assembled as an electronics project from a Heathkit PS-3 kit. Results using either source have been satisfactory.

Typical Results

Figure 3 indicates instrument response as a function of electrolyte concentration; reagent grade potassium chloride was used as electrolyte. Figure 4 shows instrument response as a function of dielectric constant. The reader may compare these data with those of Hall and co-workers (*6*) who have built a similar apparatus for student use operating at 2.0, 5.0, and 10.7 megacycles. Their paper includes a discussion of principles.

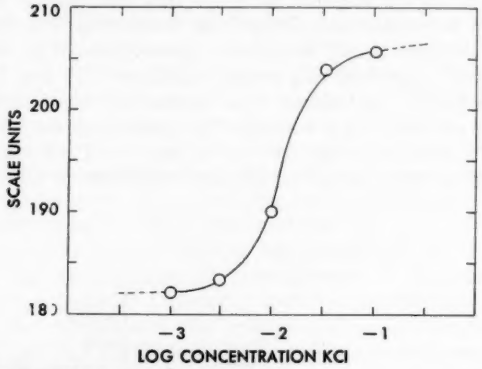


Figure 3. Electrolyte concentration response.

The authors have used the instrument described in this paper in a course in instrumental analysis with considerable success. Theory may be presented either in brief or in considerable detail; see, for example, the article by Reilley and McCurdy (*7*). The instrument yields good results with acid-base titrations in water and in non-aqueous solvents such as glacial acetic acid. The instrument is also useful in the field of binary solution analysis provided the dielectric constants of the components differ sufficiently. For this use, calibration curves are prepared by the student before an unknown is issued. Results can be duplicated to within a dial division in a range of one hundred.

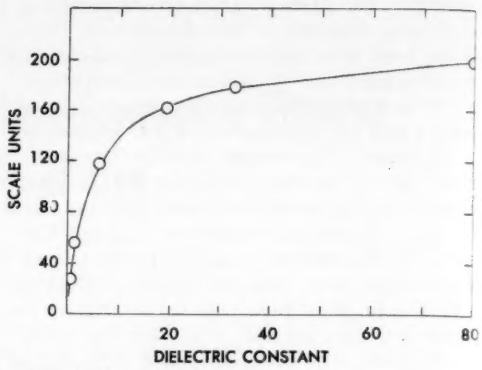


Figure 4. Dielectric constant response.

Literature Cited

(1) Blaedel, W. J., and Malmstadt, H. V., *Anal. Chem.*, 22, 734 (1950).

(2) Jensen, F. W., and Parrack, A. L., *Ind. Eng. Chem., Anal. Ed.*, **18**, 595 (1946).

(3) Scientific Apparatus and Methods, **9**, no. 1, 2–10, E. H. Sargent and Company (1957).

(4) West, P. W., Burkhalter, T. S., and Broussard, L., *Anal. Chem.*, **22**, 889 (1950).

(5) Johnson, A. H., and Timnick, A., *Anal. Chem.*, 28, 889 (1956).

(6) Hall, J. L., Gibson, J. A., Phillips, H. O., and Critchfield, F. E., J. Chem. Educ., **31**, 54 (1954).

(7) Reilley, C. N., and McCurdy, W. H., *Anal. Chem.*, 25, 86 (1953). See also the chapter by C. N. Reilley in Delahay, Paul., "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, 1954, pp. 319–54.

MCA Honors Six College Chemistry Teachers

The 1960 College Chemistry Teacher Awards of the Manufacturing Chemists' Association will be made on June 9, 1960. The following medalists were chosen from 189 nominations submitted by college and university presidents.

Reynold C. Fuson, University of Illinois, Urbana
Ben Harrison Peterson, Coe College, Cedar Rapids, Iowa
Francis O. Rice, Georgetown University, Washington, D. C.
Walter Hugo Stockmayer, Massachusetts Institute of Technology, Cambridge
Moddie D. Taylor, Howard University, Washington, D. C.
John DeVries, Calvin College, Grand Rapids, Michigan

R. T. Sanderson
State University of Iowa
Iowa City

Atomic Models in Teaching Chemistry

Continuing teaching experience with atomic models, as described briefly in THIS JOURNAL (*9*) and in greater detail in two recent educational films (*10*), has strengthened the belief that the use of such models deserves thorough consideration by all teachers of chemistry. This paper extends the discussion of atomic models briefly begun in reference (*9*).

Except as units for construction of molecular models, of which a number are commercially available and to which there are numerous literature references, relatively little on atomic models to be used separately in teaching has been published (*1–8*, *12*, *13*) since the nuclear atom was conceived in 1913. If models of atoms truly have potential value as visual aids to learning, one may well ask at once why such models are not used universally in the teaching of chemistry, now.

Possibly the major deterrent has been the impossibility of constructing a reasonable facsimile of so nebulous and dynamic a system as an atom. Coupled with this, very likely, is a reluctance to "oversimplify" so mighty an intellectual construction as the modern theoretical atom. Such oversimplification risks condemnation as "unscientific." Certainly no conscientious teacher wishes to create deliberately erroneous impressions for the sake of simplicity. Neither does he want to be labelled "unscientific."

The use of atomic models can, nevertheless, be thoroughly justified without apologies to either theoretician or student. For an atom has important qualities that can be, not *duplicated*, but *represented* with useful accuracy, in a simple model. The models described earlier (*1*) are designed to represent the three qualities: relative size, electronegativity, and valence electronic structure. The size is represented by a Styrofoam sphere, the electronegativity by its color, and the valence electronic structure by small balls glued in appropriate positions to the surface of the sphere. Surely no intelligent student will think from these models that atoms are made of Styrofoam, that sodium is red and fluorine blue, or that electrons are stationary white balls glued to the atomic surface. He will, however, be given an unequalled opportunity to visualize atoms in terms or qualities which are of major importance in determining the properties of the elements and their compounds. So great are the advantages of such atomic models in demonstrating the inherent reasonableness of chemistry that any disadvantages seem insignificant in comparison.

For lecturing to groups of one hundred or more, I have found double the usual scale (*1*), or 3 in. per Angstrom unit to be preferable—or one might use an even larger scale. On this scale, an atom of hydrogen is $2^1/_2$ in. in diameter and an atom of 2.2Å radius (Cs) can be represented by a 13 in. diameter. The details for the 37 active elements for which models can most advantageously be shown are given in Table 1. For smaller classes, the molecular model scale of 1.5 in. per Angstrom is quite satisfactory.

The valence electronic structure shown on these models is the outermost four orbitals (*s* and three *p*) with electrons (represented in the large models by

Table 1. Data for Construction of Atomic Models

Element	Sphere diameter, in. Correct[c]	Available[a]	Color[b]	No. of electrons	No. of vacancies
H	1.11	$1^1/_8$	2N	1	1
He	2.79	3	gray	0	0
Li	4.02	4	11P	1	7
Be	2.70	3	6P	2	6
B	2.46	2.5	1P	3	5
C	2.31	2.25	3N	4	4
N	2.25	2.25	7N	5	3
O	2.19	2.25	10N	6	2
F	2.16	2.25.	12N	7	1
Ne	3.93	4	gray	0	0
Na	4.62	5	12P	1	7
Mg	3.90	4	9P	2	6
Al	3.54	4	6P	3	5
Si	3.33	4	2P	4	4
P	3.18	3	1N	5	3
S	3.06	3	5N	6	2
Cl	2.97	3	9N	7	1
Ar	5.22	5	gray	0	0
K	5.88	6	12P	1	7
Ca	5.22	5	9P	2	6
Zn	3.93	4	1P	2	6
Ga	3.78	4	1N	3	5
Ge	3.66	4	2N	4	4
As	3.57	4	4N	5	3
Se	3.48	4	5N	6	2
Br	3.42	4	7N	7	1
Kr	5.64	6	gray	0	0
Rb	6.33	...	12P	1	7
Sr	5.76	6	10P	2	6
Cd	4.44	5	3P	2	6
In	4.32	5	1P	3	5
Sn	4.23	5	0 (yellow)	4	4
Sb	4.14	5 or 4	1N	5	3
Te	4.05	4	2N	6	2
I	3.99	4	3N	7	1
Xe	6.27	...	gray	0	0
Cs	6.75	...	12P	1	7
Ba	5.94	6	10P	2	6
Hg	4.47	5	1P	2	6
Tl	4.44	5	Y	3	5
Pb	4.41	5	Y	4	4
Bi	4.38	5	Y	5	3
Rn	6.42	...	gray	0	0

[a] Star Band Co., Portsmouth, Virginia.

[b] 12P is red, 7P is orange, Y is yellow, 7N is green, and 12N is blue. Colors 8P to 11P obtained by mixing 12P with 7P; 1P to 6P, by mixing Y with 7P; 1N to 6N, by mixing Y with 7N; 8N to 11N, by mixing 7N with 12N. The electronegativity range from low to high is represented by the range in hues from red through yellow to blue.

[c] Based on nonpolar covalent radius.

$^3/_4$ in. diameter white Styrofoam balls and by $^3/_8$ in. diameter wooden or plastic balls or beads in the smaller models,) distributed as they are in valence, i.e., no pairing until each orbital is half full. To those who would object that an atomic model ought to show the structure of the ground state rather than the valence state, it may be observed that atoms are in the ground state—where it differs from the valence state—only when in the form of unexcited monatomic vapor. What is the value of showing a boron atom, for example, with an outer $2s^2$, $2p$ configuration, when it never has

Figure 1. The combination of hydrogen with oxygen occurs as predetermined by the nature of the atoms. (Lecture models, left to right: in hands, H and O; on table, H_2O, H_2O, H_3O^+; and OH^-.)

that configuration either in elementary boron under normal conditions or in any of its compounds? How much more useful to explain the difference, but to show the sp^2 hybrid orbitals, directed toward the corners of an equilateral triangle, together with the fourth empty orbital. Then a student can see at a glance the capacity of boron to form three planar ordinary covalent bonds, and having done so, to act as electron acceptor (thereby becoming tetrahedral). The orbital vacancies are represented by $^3/_4$ in. diameter black Styrofoam balls. A pair of black balls represents a vacant orbital, whose position is arbitrary on the model because only orbitals containing electrons may be regarded as having or influencing directional properties of bonds.

Unfortunately, suitable representations of valence electronic structure in transition metal atoms have not yet been devised. For this reason only models of inert-shell and 18-shell elements are discussed herein.

Physical Properties of the Elements

The common physical properties, such as density, melting point, boiling point, and electrical conductivity, are not the properties of individual atoms or molecules. They are the properties of *aggregates* of atoms and/or molecules. The nature of these aggregates, however, is the consequence of the nature of their atoms, and from this viewpoint, atomic models can be helpful in explaining the physical properties of the elements.

Perhaps the most difficult question to answer satisfactorily on an elementary level is why some atoms form metallic crystals instead of the kinds of aggregates that would reasonably be expected from consideration of their capacity to form ordinary covalent bonds. For example, why does not lithium, with its single outer electron, exist as diatomic Li_2 molecules?

In fact, as monatomic lithium vapor is cooled, Li_2 molecules do form, but these combine on further cooling to give a crystalline solid in which each interior atom has 14 close neighbors, 8 in closest contact and 6 more a little farther distant. By way of explanation, one can only point out that in Li_2, the "expected" molecule, each atom has three totally unoccupied outermost orbitals, whereas in lithium metal, all orbitals are presumably involved in the metallic bonding. That this produces a more stable aggregate is evidenced by the heat of atomization of metallic lithium, 38 kcal, compared to 12 kcal for the gram atomic heat of atomization of Li_2. In other words, a metallic crystal of lithium is more stable than a collection of the same atoms in the form of diatomic molecules by about 26 kcal per gram atomic weight of lithium. The metallic state seems consistently to result when the ratio of valence orbital vacancies to electrons is relatively high. One might then account for the "stair-step" division between metal and nonmetal (*11*), in the periodic table, as a consequence of (*a*) diminishing ratio of vacancies to electrons in the outer octet from left to right, and (*b*) increasing availability of outer *d* orbitals from top to bottom. Trend (*a*) is toward diminishing metallic character and trend (*b*) toward increasing metallic character.

As soon as the atoms have sufficient outer electrons to utilize all vacancies in conventional covalent bonding, the metallic state disappears. Thus beryllium is less metallic than lithium, boron neither metallic nor conventionally covalent but intermediate in nature, and carbon strictly covalent. From carbon on, the atomic models can serve quite specifically to explain, or at least rationalize the states of aggregation of the elements in terms of normal covalence.

The diamond structure of carbon is easily predictable from the carbon atom model, which shows each carbon able to form four single covalent bonds directed toward the corners of a regular tetrahedron. The graphite form seems quite different, but careful study of the diamond structure will disclose nonplanar condensed 6-membered rings therein, which, if deprived of their covalent bonds to the roughly parallel (but nonplanar) layers of condensed rings, could easily change to the planar layers of graphite. The reverse procedure, forming diamond out of graphite, would require the forcing of the layers of condensed rings much closer together. This can actually be done, but only at high temperatures and very high pressures.

In nitrogen, the capacity of each atom to form three normal covalent bonds, as shown by the model, is evidently utilized completely in the formation of one triple bond, in N_2. Similarly, the capacity of oxygen atoms to form two covalent bonds is utilized completely in the formation of O_2 molecules. The models show that the observed diatomic molecules are perfectly reasonable. In neither element, unfortunately, could one predict from the model that multiple bonding and diatomic molecules would take preference over polymerization through single bond formation. One may explain that with smaller atoms, such as those of carbon, nitrogen, and oxygen, the formation of single bonds brings other half-filled orbitals in contact, thus causing bond multiplicity, whereas in larger atoms such as those of silicon, phosphorus, and sulfur, the other

half-filled orbitals when two atoms are joined by a single bond do not overlap enough for significant multiple bonding, and polyatomic molecules joined together by single bonds occur instead of diatomic molecules joined together through multiple bonds.

A model of an atom of fluorine shows very clearly that F_2 molecules can form, but no orbitals other than the ones involved in the single covalent bond can overlap since all the others are full and can only repel one another. Incidentally, this explains the unexpectedly low dissociation energy of diatomic fluorine. Just as in carbon, nitrogen, and oxygen, other orbitals of fluorine are in position to overlap when a single bond is formed, but in fluorine these orbitals differ in being full, and therefore they can only repel one another, thus weakening the bond.

Having used the models to show at least the reasonableness of the states of aggregation exhibited by the elements in their normal condition, one can then proceed to point out the direct relationship between the structure of the aggregates and the physical properties. Models of the aggregates, as shown in (*1*), are of course nearly indispensable in this teaching. The metallic properties of lithium and beryllium are of course the consequence of their structure. The smaller size of beryllium atoms and their more compact packing make inevitable a greater density, and higher melting and boiling points than lithium. The compact clusters of boron atoms are likewise consistent with its hardness and high melting and boiling points. Similarly, the properties of diamond and graphite reflect their "giant molecule" nature and the fact that melting and vaporization cannot occur without the breaking of strong covalent bonds. The striking jump in properties from carbon to nitrogen is obviously the consequence of nitrogen being diatomic instead of polymeric like carbon. Similarly, the very low melting and boiling points of oxygen and fluorine indicate the expected repulsive forces among their molecules. The important point to emphasize in all such discussion is that the physical properties of the elements are neither accidental nor mysterious, but are always the inevitable and reasonable consequence of the particular qualities of their atoms.

Formation and Properties of Compounds

Even more important in chemistry is the prediction of compounds and their properties from a knowledge of the component atoms. Here the new atomic models, especially when used in conjunction with the new molecular or crystal models, can give teachers a powerful new explanatory tool. For examples, let us consider in detail the compounds, sodium chloride, water, and methane.

A model of a sodium atom shows it to be relatively large, very low in electronegativity, and capable of forming only a single covalent bond. Certainly a student can be told these facts, but seeing the model can be so much more satisfying. He can understand from the large size that the outer electron is not very tightly held, and the fact of a low ionization energy is expected. The red color of the model shows the electronegativity to be very low, as should be expected from the fact that the atom does not even hold its own outer electron tightly. The presence of three empty outer orbitals is also to be noted on the model, but with the low electronegativity, sodium is not expected to use these orbitals readily to accept outside electron pairs. However, the high ratio of vacancies to electrons in the outer shell strongly suggests a metallic state for sodium under ordinary conditions. Any student, by examination of this model and with an understanding of what it represents, can predict that bonds of sodium atoms to almost any other element will be appreciably polar, leaving the sodium at least partially positive.

Examining now a model of an atom of chlorine, a student can see from its much smaller size, despite 17 electrons instead of 11, that the atom is much more compact and thus evidently holds its electrons tightly. The single vacancy in the outer shell shows at once that only one covalent bond can ordinarily be formed per atom, but if the atom holds its own electrons tightly it can be expected to attract an outside electron strongly if a vacancy exists to accommodate it. The blue-green color confirms this expectation of high electronegativity. The atom is seen also to have three outer electron pairs, but as the atom has high electronegativity, these are not expected to be donated readily in formation of coordinate bonds.

Study of the two atomic models makes quite inescapable the prediction that an encounter between a sodium atom and a chlorine atom will result in their joining through a highly polar covalent bond. The chlorine here will become so negative as to be considered, for practical purposes, to have gained full control of the shared electrons, thus becoming a chloride ion, leaving the sodium as a sodium ion. When large numbers of such ions come together, the laws of electrostatics result in an arrangement of highest possible stability, with each ion as far as reasonably possible from other like ions but as close to the oppositely charged ions as possible. In this particular compound the familiar cubic structure is the result. The strong electrostatic forces render the crystal high melting and the liquid high boiling, and yet soluble in strongly solvating liquids such as water. The point to emphasize here is that sodium chloride is not an inexplicable wonder of nature but merely the inevitable consequence of the inherent nature of sodium and chlorine atoms. With the models, one does not just tell students these facts, but reinforces the telling by demonstration of visible atoms, the most significant properties of which are visually represented.

The next example is water. A model of a hydrogen atom suggests that it is relatively very small, that it has a moderately high electronegativity, and that it is able to form one and only one covalent bond. A model of an oxygen atom shows that it is much more electronegative than hydrogen, can form two covalent bonds, and has two completely filled orbitals that might be utilized in the formation of coordination bonds. The angle between the two ordinary covalent bonds it can form is predetermined in the oxygen atom, and visible in the model.

The point is that the water molecule, a model of which should also be used, can be demonstrated, by means of the oxygen and hydrogen models, to be

directly the consequence of the nature of oxygen and hydrogen atoms. The geometry of the water molecule, with its hydrogen atoms attached to the oxygen at an angle of 105.5°, can readily be seen as the result of the orientation of orbitals in the oxygen atom. The polarity of its bonds (shown vividly in the molecular model of water by the green negative oxygen and the orange positive hydrogen), is seen to be inevitable, in view of the much higher electronegativity of oxygen (blue-green) than of hydrogen (yellow-green). The ability of water to become coordinated to electron acceptors such as cations reflects both the presence of outer-filled orbitals, as shown on the oxygen model, and the negative charge on oxygen, as implied by the electronegativity difference shown by the atomic models, and confirmed by the green color of the oxygen in the model of water. This coordinating ability of course explains the protonic bridging (hydrogen bonding) in liquid and solid water and thus their physical properties, and together with the water's molecular polarity explains the water's action as solvent for polar and ionic substances.

The third example, methane, can be explained very clearly in terms of models of carbon and hydrogen. The carbon model has four half-filled orbitals directed toward the corners of a regular tetrahedron, and a yellow-green color indicating an electronegativity just a little higher than medium. The hydrogen model, with its single half-filled orbital, is only slightly more yellow, indicating an electronegativity close to that of carbon but a little lower. Obviously, from these models, the simplest compound of carbon and hydrogen must have four hydrogen atoms attached to one carbon atom, per molecule, and the shape of the molecule must be tetrahedral. The bonds can be only slightly polar, shown in an appropriate molecular model of methane by yellow hydrogen atoms but faintly greenish carbon. The symmetry, even if the bonds were polar, would indicate the probability of low intermolecular attraction, and this of course is characteristic of methane, a very volatile substance.

The relatively small size of the carbon atoms shows not only that the carbon-hydrogen bond should be exceptionally strong, but also that very stable carbon-carbon bonds can form. These carbon-carbon bonds in a hydrocarbon are not expected to be weakened, or even materially influenced by the hydrogen-carbon bonds, which would not be the case if the latter were substantially polar. The models of carbon and hydrogen atoms thus can serve to help explain the occurrence and possibilities of such an enormous number of hydrocarbons.

The teaching of chemistry has been accomplished, with some success, for generations, without the help of atomic models. How much more meaningful it could have been, and can be now, with the help of these new aids to visualization. In the face of the rapidly accelerating expansion of empirical chemical knowledge, no possible help to student understanding of the fundamentals should be overlooked. What could possibly be more fundamental in chemistry than the cause and effect relationship between the qualities of individual atoms and the properties of their chemical combinations?

Support of this work by the National Science Foundation, Course Content Improvement Section, is gratefully acknowledged.

Literature Cited

(1) Brooks, W. G., J. Chem. Educ., **24**, 245 (1947).
(2) Dodson, V. H., J. Chem. Educ., **33**, 529 (1956).
(3) Evans, W. L., and Day, J. E., J. Chem. Educ., 1, 100 (1924).
(4) Fowles, G. W. A., J. Chem. Educ., **32**, 260 (1955).
(5) French, S. J., J. Chem. Educ., **10**, 564 (1933).
(6) Hall, G. A., J. Chem. Educ., **24**, 564 (1947).
(7) Holness, H., *School Sci. Rev.*, **25**, 38 (1943).
(8) Pouleur, A. L., J. Chem. Educ., **9**, 301 (1932).
(9) Sanderson, R. T., J. Chem. Educ., **36**, 507 (1959).
(10) Sanderson, R. T., (*a*) "Atomic Models, Valence, and the Periodic Table"; (*b*) "New Models of Molecules, Ions, and Crystals: Their Construction and General Use in Teaching Chemistry"; films available from Bureau of Audio-Visual Instruction, Extension Division, State University of Iowa, Iowa City, Iowa.
(11) Sanderson, R. T., J. Chem. Educ., **34**, 229 (1957).
(12) Scott, E. C., J. Chem. Educ., **8**, 1845 (1931).
(13) Waring, M. G., *Trans. Kans. Acad. Sci.*, **43**, 363 (1940).

D^{t*}

F, now the dentists say,
Forms D^t that won't dK.
Let's formulate this new found truth:
$dFd\phi sdKD^2$.

Just how dFdK prevents
Remains for more experiments.
But it's a fact you can't gainsay:
$D^t + Fd\phi dK$.

$D^t - dFdK$
Though care may keep dK away
And some believe that this is true:
$D^2 + C_{12}H_{22}O_{11}dKs_2$.

Some also say Ca and P
With just a trace or more of D
Will keep D^t from caries free.
Say $\sqrt{s}$ "dKLb".

But if dKD^2 a man
It is well known a dentist can
With Ag, Hg, and Au
Fix up D^t (4u2 chew).

Now if you give dK no care
D^t go faster than your hair.
This warning I will leave with you:
$d\sqrt{D^2}\,LdK_2$

Gerald J. Cox
University of Pittsburgh
School of Dentistry

* $(Dee)^{teeth}$ for non-punners and Chem Gem ignorers.

John A. Ricketts
DePauw University
Greencastle, Indiana

A Laboratory Exercise Emphasizing Deductive Chemical Reasoning

To stimulate the student experiments in the beginning, chemistry laboratory should not only demonstrate a chemical principle and illustrate laboratory techniques, but also offer a mental challenge. The desirability of such experiments has been discussed by both Blick[1] and Young.[2] In this laboratory this is the student's first experiment. Essentially it involves the techniques of qualitative analysis. It differs from the exercise described by Summerbell[3] in which an ion foreign to the classical qualitative scheme is given the student after he has familiarized himself with the procedure, and that described by MacWood[4] in which the behaviors of nine different solutions are studied with respect to each other. The student observes the chemical behavior of the aqueous solutions of five pure nitrate salts toward several common laboratory reagents. From his observations he synthesizes a scheme of analysis that can be used to identify the components of a mixture containing any combination of the five salts. The student then tests his procedure by analyzing an unknown mixture.

Outline of the Experiment

Since the most common laboratory blunders in qualitative analysis are incomplete precipitation of a particular ion or insufficient washing of a precipitate, the proper technique of precipitation and filtration is emphasized in a preliminary exercise. Silver chloride is precipitated from silver nitrate solution by the addition of copper(II) chloride solution. The resulting mixture is filtered, and the precipitate is washed until the washings are free of the copper(II) ion, the presence of which is detected by the formation of the copper(II)-ammonia complex upon the addition of ammonium hydroxide to the washings.

The prime purpose of this experiment is deduction from observation; consequently, the stock solutions of the five nitrate salts are simply labeled I, II, III, IV, and V. The salts are silver nitrate, mercury(I) nitrate, cadmium nitrate, aluminum nitrate, and barium nitrate. The stock solutions contain 10 mg of cation per ml of solution. The laboratory reagents are dilute solutions (6*M*) of sodium hydroxide, hydrochloric acid, sulfuric acid, nitric acid, and ammonium hydroxide.

The student performs the following test tube reactions—twenty-five in all. Separate 3 ml samples of each of the reagents are added to individual 3 ml portions of each of the five nitrate salts.

To those test tubes in which a precipitate appears upon adding hydrochloric acid, excess ammonium hydroxide is added with stirring. If any of these precipitates dissolves, the solution is neutralized with nitric acid.

To those test tubes in which a precipitate appears upon adding either ammonium hydroxide or sodium hydroxide, an excess of the precipitating base is added to determine whether or not the precipitate is soluble on excess of the base. To those precipitates that dissolve, nitric acid is added until the precipitate that first reforms redissolves.

The student records his observations in his notebook in a five-by-five array. (A typical square is shown here.) From these observations he devises a method of analysis for a mixture that might contain any combination of the five salts. His procedure is approved before he is given an unknown mixture. It is particularly effective when a student has an incorrect procedure to have him try his scheme on a solution—a solution compounded by the student himself—that contains all five of the ions.

Reagent / Solution	HCl	H_2SO_4	NH_4OH	NaOH	HNO_3
I $AgNO_3$	white ppt. sol. NH_4OH reppt. with HNO_3	no reaction	brown ppt. sol. excess NH_4OH	brown ppt.	no reaction
II $Hg_2(NO_3)_2$	white ppt. turns black addn. NH_4OH	white ppt.	black ppt.	black ppt.	no reaction
III $Cd(NO_3)_2$	no reaction	no reaction	white ppt. sol. excess NH_4OH	white ppt.	no reaction
IV $Al(NO_3)_3$	no reaction	no reaction	white gelatinous ppt.	white ppt. sol. excess NaOH	no reaction
V $Ba(NO_3)_2$	no reaction	white ppt.	no reaction	no reaction	no reaction

A typical compilation of student observations.

Conclusion

This particular laboratory exercise has been performed by about 120 students including 80 teachers of science in elementary and junior high schools. Seventy-five per cent of these analyzed their mixtures correctly; each mixture contained at least three of the five ions. Most mistakes in the analyses were in the detection of cadmium and aluminum. This experiment gave the student a sense of accomplishment from the beginning chemistry laboratory periods before having had much

[1] Blick, D. J., J. Chem. Educ., **32**, 264 (1953).
[2] Young, J. A., J. Chem. Educ., **34**, 238 (1957).
[3] Summerbell, R. H., Lestina, G., King, L. C., and Neumann, H. M., J. Chem. Educ., **32**, 475 (1955).
[4] MacWood, G. E., Lasseltre, E. N., and Breem, G., J. Chem. Educ., **17**, 520 (1940).

formal instruction. In addition it seemed to allay the student's fear of the chemistry laboratory. Later when the student has gained enough chemical maturity, the correct scheme is explained by means of chemical equations. This particular laboratory exercise should find profitable application in the high school laboratory since even those students who had taken high school chemistry enjoyed the experiment.

Walter R. Carmody
Seattle University
Seattle 22, Washington

Dynamic Equilibrium:

A simple quantitative demonstration

Dynamic chemical equilibrium and the part mass action plays in its attainment are concepts that present some difficulty to the beginning student. The mechanism by which a chemical reaction comes to equilibrium is not apparent to the student when he observes even the simplest of such reactions. It is possible, however, to demonstrate the mechanism by which a physical equilibrium is attained and then the analogy between it and the attainment of a chemical equilibrium can be drawn.[1] Although it has been criticized by W. Hered[2] the author believes that this method is very effective in helping the student visualize the mechanism of a chemical dynamic equilibrium.

The rough qualitative demonstration of a physical equilibrium involving the simultaneous transfer of a liquid between two vessels has been described by Sorum[3] and by Kauffman.[4] The containers used for the liquid were large beakers or crystallizing dishes and the transferring "dippers" comprised evaporating dishes or beakers of varying sizes. The author has found that this sort of demonstration can be greatly improved and made quantitative by employing graduated cylinders as containers for the liquids and "homemade" pipets as the dippers. This arrangement permits the taking of data and the preparation of curves to illustrate the course of a single reaction and also that of an equilibrium. Quantitative expressions for the rate and for the equilibrium can be developed, and then the similarity between these expressions and the corresponding expressions for a chemical reaction can be shown. As a result the analogy between the attainment of a chemical equilibrium and the attainment of a physical equilibrium is clearly drawn.

Apparatus

From the 100-ml cylinder stock a pair is selected that have precisely matched graduated scales. These may be used as they are, or they may be cut off to a more convenient height; i.e., at the 90-ml mark. The "dippers" are pairs of glass tubes that are partially closed at one end so that they may serve as pipets. When such a pipet is immersed in a liquid so that the end touches the bottom of the container, the volume of the liquid entrapped is directly proportional to the height of the liquid in the container. One 9-mm tube and one 12-mm constitute a suitable pair; also two 10-mm tubes. The *relative* cross sections of the pipets in each pair may be determined by measuring the volume of liquid dipped by each pipet from a beaker of water kept at a constant level. To increase the precision of the result the volume supplied to a graduated cylinder by four or five dips may be measured in each case. This may be done before the demonstration, or it may be made a part of the demonstration.

Demonstration of the Rate Process

One of the graduated cylinders is filled to the 80-ml mark with colored water, and it is pointed out that the scale reading not only indicates the volume of the liquid but also is a measure of the height of the liquid in the cylinder. A pipet tube (8 to 12 mm in diameter) is dipped to *the bottom* cylinder, the upper end is closed with a finger, and the containing liquid pipetted out. The volume of the liquid remaining in the cylinder is then read (to the nearest ml) and recorded on a graph of volume versus number of dips drawn on the blackboard. The operation is repeated until there is practically no water remaining in the cylinder. A smooth curve is drawn through the points on the graph, and the relationship between the slope and the height discussed. The equation for the rate of transfer of the liquid is then presented,

$$R_v = (h)(a)$$

in which R_v represents the volume of liquid transferred per dip of the pipet, h represents the height of the liquid in the cylinder, and a represents the cross-sectional area of the pipet. It is pointed out that the height of the liquid is the variable factor in the equation and that the rate of transfer of the liquid varies with the height and is reduced to zero as the height of the liquid is reduced to zero.

The mass action expression for a first order reaction is written,

$$r = (c)(k)$$

[1] This demonstration was designed for presentation at the Summer Institute for High School Teachers of Science and Mathematics conducted by Seattle University and sponsored by the NSF. It was voted a "most satisfying" demonstration by the members of the seminar on lecture demonstration.

[2] HERED, W., J. CHEM. EDUC., **27**, 542 (1950).

[3] SORUM, C. H., J. CHEM. EDUC., **25**, 489 (1948).

[4] KAUFFMAN, G. H., J. CHEM. EDUC., **36**, 150 (1959).

and the significance of each term discussed. The analogy then may be drawn between the two variables, height and concentration, and the cause for the declining rate during the course of a chemical reaction explained.

Demonstration of Dynamic Equilibrium

The pair of matched graduate cylinders is clamped on the desk in a position most suitable for the simultaneous transfer of liquid from each to the other. One of the cylinders is filled to the 80-ml mark with colored water.

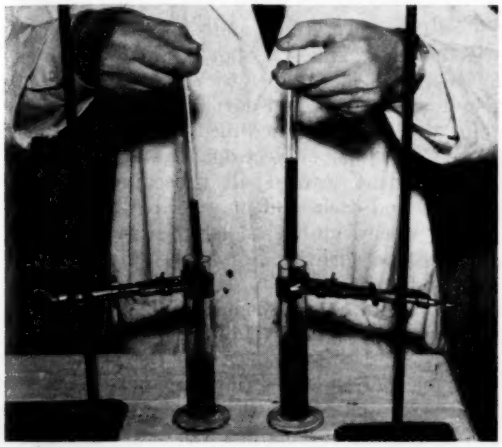


Figure 1. Simultaneous transfer of liquid.

The larger of a pair of immersion pipets is placed in this cylinder and the smaller in the empty cylinder. Closing the tops of the pipets, one transfers the contents of each simultaneously to the other cylinder (Fig. 1). The volume of liquid in the second cylinder is read, and this is recorded on a graph of volume versus number of exchanges (Fig. 2). The operation is repeated (twenty times or more) until no change in volume can be detected during three or four successive exchanges. A smooth curve is drawn through the points on the graph, and the shape of the curve is explained in terms of the operation of the two variables and their effect on the two opposing rates.

The expression for the dynamic equilibrium in terms of the final (equilibrium) *relative* heights and *relative* cross sections of the pipets,

$$(h_1)(a_1) = (h_2)(a_2)$$

is developed, and the equality of the two checked using the experimental data. Sample results are shown in the accompanying table. In order to demonstrate more convincingly the equality of the two opposing rates at

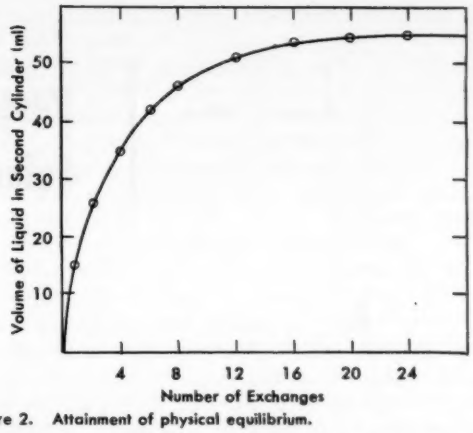


Figure 2. Attainment of physical equilibrium.

equilibrium, the pipets are dipped again into the cylinders and the enclosed liquids pipetted into two 10-ml graduate cylinders and the volumes recorded. The results usually are quite convincing to the students.

Table 1. Sample Results of Physical Equilibrium Demonstration

	Cylinder no. 1	Cylinder no. 2
Height, equilibrium (relative)	25	55
Area of pipet (relative)	2.24	1.00
Product (height)(area)	56	55

The equality of reaction rates for an analogous chemical equilibrium is written,

$$(c_r)(k_1) = (c_p)(k_2)$$

in which c_r and c_p represent the equilibrium concentrations of the reactant and product respectively.

It is to be noted that the heights of the liquids in the cylinders are somewhat greater when the pipets are immersed than they are when the readings are taken. The *relative* increase in height in the cylinder containing the pipet of larger diameter is slightly greater than that in the other cylinder. As a result the relative rate of transfer as measured by the product (height)(area), is usually slightly larger for the pipet with the larger diameter. If one desires to eliminate this error, one can either record the volume (height) readings each time with the pipets immersed, or one can originally determine the relative cross sections of the pipets by a method that involves their immersion in equal volumes of liquid contained in the two cylinders.

The analogy between the variables of the physical equilibrium and those of the chemical are again drawn and the mechanism by which a chemical reaction reaches equilibrium finally elucidated.

U. S. colleges and universities increased their scientific research and development 80 per cent between 1954 and 1958, a National Science Foundation study shows. Comparisons with a 1953–54 study show that Federal expenditures for research and development in colleges and universities proper increased 55 per cent during the same period—from $140.7 million to $217.9 million.

Robert L. Silber
Central High School
Evansville, Indiana

Research Experiences Attract Talented High School Students

Are you looking for a method of stimulating interest and challenging the academically-talented students in chemistry on the high school level? Would you be interested in having these students make some contribution to the field of science? Would you like to give your students research experiences to help determine their potentialities and to help them find out whether a career in chemistry or science is really for them?

Many schools have nothing to offer the academically-talented student in science beyond the regular class work. Some schools offer additional work to attempt to challenge these students. Others are offering advanced courses to further their knowledge, but often the classes may be too small to convince the administration of their value. Science fairs could be the answer in some situations. The answer to the above questions and statements could be found in a basic research program involving students at the high school level.

Superior students will jump at the chance to have experiences in basic research. How can such a program be accomplished? What are the results?

In December of 1956, such a program was inaugurated in Evansville, Indiana, at Central High School. In the third floor chemistry laboratory, a group of five students were selected, based on high school scholastic records, IQ's, and professed interest. Each of these had taken courses in biology and chemistry and was enrolled in physics. The research involved the ascertaining of the number and kinds of free amino acids in a series of fruits with particular direction toward the possibility of detecting the suspected presence of two new amino acids. A grant from the National Institutes of Health was obtained to support the work.

The employment of the students involved several conditions. First, they could only work after school, two evenings per week. Second, they must consider this work their most important after-school activity, with a very limited number of reasons accepted as excuses. Third, they would be paid 35¢ per hour, enough to buy lunch and pay their bus fares.

While waiting for ordered equipment and supplies, the students began a search of the literature at a local college to determine what had been done in the field. Orientation sessions were held the two evenings per week to give them background in the work and acquaint them with the various processes involved.

Upon arrival of equipment, work was begun. Several varieties of fruit were purchased and the processing started. It was necessary first to grind the fruit with ethyl alcohol in a blender, then filter the material to remove the fiber. Ion-exchange columns were employed to remove the amino acids. The ammonia was removed from the extract, and the extract lyophylized, to remove the water. A spot of the lyophylized extract was placed on paper to be separated by paper chromatography.[1] Upon development of the chromatograms, the spots were identified. These in many cases were verified by paper electrophoresis.

Each student learned all procedures. After the training period each student was able to take a fruit and carry it through the whole process with the exception of the final identification of the amino acids.

The first year was not without many difficulties. Working only three and one half hours after school, two days per week, presented difficulty in the timing of chromatograms. Many phases of the project seemed only to be started when time ran out. Few visible results were obtained in the first year. However, a four-year renewal of the grant was received, for a much larger amount, and the project was continued with new students and additional equipment.

The second research team consisted of seven students. The work was carried on in the same fashion as before, after a period of orientation. After the school year ended, this team was able to work full time during the summer for a six-week period. This, of course, kept the students interested, busy, and partially solved the problem of searching for summer employment. (They had been given a raise to 50¢ per hour.)

The 1958–59 research team consisted of nine students. Additional equipment such as a *p*H meter, fraction collector for ion-exchange chromatography, analytical balance, chromatography drying oven, etc., were now available. Some of this equipment was made locally by the industrial arts department. This team was able to work eight weeks during the summer.

In addition to the laboratory work, each team had an extensive field trip taken on time released from school. Approximately 700 miles and five days were necessary to visit an agriculture experimental farm, the research laboratories of a large pharmaceutical company, a heavy industry, a steel mill, Argonne National Laboratory, and several museums in Chicago. The trip was planned to acquaint the students with research facilities in various types of industries and to see science applied in many situations. The students were surprised to see that many of the techniques they had used themselves were employed in the larger research laboratories. They felt a sense of pride whenever they were able to converse with scientists in those laboratories.

Benefits from the Program

What has been the result of such a project? A total

[1] Irreverre, F., and Martin, W., *Anal. Chem.*, **26**, 257–60 (1954).

of seventeen students has graduated with this experience (some were selected as juniors and remained on the team two years). Of these seventeen, fourteen are undertaking science or science-related fields of study in college.

A follow-up study by means of personal correspondence indicates that the experience better prepared the students for college.

A third result has been the submission and acceptance for publication of a paper describing the research done on the free amino acids derived from 32 fruits.

The fourth consequence, although somewhat unmeasureable, was the closeness of the instructor with the students. Greater friendships were built, and much more guidance done, in this close association, than in ordinary classroom situations. The students, even after several years in college, return to see how the new team is progressing and reminisce about their experience while on the team.

Still a fifth result is obtained by such an experience. Many science teachers feel that they would like to do some research but have no means of support for such a project. This project provides the funds for equipment, travel, compensation, and supplies. This helps the teacher with a source of extra income and in some instances, may keep a teacher in the classroom instead of seeking other higher-salaried opportunities.

A sixth beneficial aspect of such a program lies in the anticipation and striving of younger students who are desiring a place in such a project. Many more applications are always on file than there are positions available.

Two more years remain in the grant, and two new teams will be started. Anticipation is great for these two years.

Chem Ed

LETTERS

To the Editor:

I would like to comment briefly on two items appearing in the January, 1960, issue of the JOURNAL OF CHEMICAL EDUCATION.

In Dr. Alyea's Demonstration Abstracts (24s-24-135s) appears the statement that potassium ferrocyanide is recommended for the ferroxyl test. Actually this test is carried out in practice with the ferricyanide. The literature recommends ferricyanide, and the originator of the test originally used the ferricyanide.

The article by Badgett and Stansbury on an apparatus for handling liquified gases describes a piece of equipment which is similar to "Gas Liquefier and Reflux Condenser" currently being offered by Aloe Scientific Co. of St. Louis. This apparatus was invented by me in 1956 and is patent pending. The apparatus is, however, not vacuum insulated, but consists of thick glass instead. This apparatus may be used as a reflux condenser for gases readily liquefiable by dry ice solvent mixtures, such as ammonia. In fact, it is very convenient to carry out ammonolyses with the equipment. The unit is also convenient for distillation when a supply of running water is not on hand. In such a case, regular ice is used for the cooling media, and the unit is partially filled so that the melting ice will not spill.

MARVIN S. ANTELMAN,
CHEMICAL CONSULTANT

PROVIDENCE 6, RHODE ISLAND

To the Editor:

With regard to the use of chromic acid in the cleaning of laboratory glassware, the truth probably falls somewhere between the two extremes as quoted by your correspondent.

For routine cleansing of glassware chromic acid mixture provides a quick and convenient method. Unfortunately, it is very difficult to remove the last traces of chromium from the glass. In my experience even 15 washings with distilled water and a steam treatment do not suffice; chromium can still be detected polarographically. This is, of course, fatal where the cleaned apparatus is to be used for conductivity work. In my work on adsorption I have found fuming nitric acid the best cleaning agent, as it is easily removed by heat. This does not mean that I would unconditionally recommend the use of fuming nitric acid by students.

F. FRANKS

BRADFORD INSTITUTE OF TECHNOLOGY
BRADFORD 7, ENGLAND

To the Editor:

Re the letter from Crayton M. Crawford in the March, 1960, issue of THIS JOURNAL.

I have used chromic acid-sulfuric acid cleaning mixture for years, and have yet to find anything else equal to it as a *general* purpose glass cleaner. I have in my possession, pieces of apparatus which have been subjected to dozens, if not hundreds of cleanings, sometimes undergoing a soaking period of a week at a time, and I have never yet seen any evidence of etching of the glass from this treatment. I will add, however, that I have always used the mixture at room temperature, and cannot vouch for its action while hot.

WALLIS G. HINES

AURORA COLLEGE
AURORA, ILLINOIS

John R. Sampey
Furman University
Greenville, South Carolina

Chemical Research in Liberal Arts Colleges, 1952–59

The last three years have witnessed a surge of increased interest in chemical research in liberal arts colleges. In an earlier study[1] 162 colleges had 736 articles abstracted in *Chemical Abstracts* during the five-year period, 1952–56. The present report tabulates 1120 articles from 231 colleges during the eight-year span, 1952–59. The addition of 69 liberal arts institutions to those engaged in chemical research during the last three years is significant, and the increase of 384 publications reflects further the growth of the idea of research as an integral part of the liberal arts program.

Another approach to the increased interest of liberal arts colleges in research may be gained by noting that, in 1952, 53 colleges had 104 articles abstracted in *CA*, whereas in 1959 the numbers had climbed to 80 colleges with 160 abstracts in this key publication to the world's chemical literature.

Research activity, however, remains concentrated in a relatively few colleges, for 37 institutions account for 785, or 70%, of the total publications for 1952–59 (Table 1). These 37 colleges averaged one or more articles a year. Another 29 institutions had four to seven articles during the eight years, for a combined output of 149 articles (Table 2).

Table 1. Liberal Arts Colleges Averaging One or More Articles a Year in CA for 1952–59

Alfred	13	Haverford	19
Amherst	81	Marshall	9
Antioch	42	Miami (Ohio)	11
Augustana	8	Morgan State	8
Brooklyn	92	Mount Holyoke	34
Calvin	9	Mt. Mercy	13
Canisius	24	Oberlin	23
Carleton	9	Pomona	24
Carson-Newman	25	Providence	16
Centenary	10	Queens	17
C. of Holy Cross	11	Reed	20
C. of Wooster	12	Smith	31
DePaul	29	Southern Illinois	25
Fisk	18	St. Joseph (Md.)	10
Florida Southern	12	Tex. State C. Women	11
Franklin and Marshall	11	Trinity (Tex.)	12
Furman	41	U. of Richmond	13
Grinnell	9	Vassar	10
		Wesleyan (Conn.)	24

[1] SAMPEY, J. R., J. CHEM. EDUC., **34**, 352 (1957).
[2] SAMPEY, J. R., *Industrial Development 127*, "The Blue Book of Southern Progress," **1959**, p. 8.

Table 2. Liberal Arts Colleges with 4 to 7 Articles in CA, 1952–59

Abilene	5	Nazareth	4
Agnes Scott	5	New Mexico Highlands	4
Bates	4	Ohio Wesleyan	4
Bethany	4	St. Ambrose	5
C. of St. Thomas	6	St. Joseph (Conn.)	4
Connecticut	6	St. Olaf	6
Denison	5	St. Peters	4
DePauw	5	Texas Southern	7
Fresno State	5	Trinity (Conn.)	6
Hope	5	Wabash	6
John Carroll	4	Wellesley	5
Lebanon Valley	6	Wheaton	7
Linfield	4	Woodstock	4
Monmouth	6	Xavier	5
Mt. Union	4		

Additional evidence for the concentration of research in a few institutions is seen in the fact that forty per cent of the colleges (92 of 231) are credited with only one publication during the eight years, 1952–59. The 9th Edition (1959) of the "College Blue Book" has been used to determine the liberal arts status of the colleges. Several institutions passed from the ranks of liberal arts colleges to those having professional schools during the last three years.

While liberal arts colleges constitute the largest unused research potential in the country, the publications cited in this study are not insignificant. Measured quantitatively the 1120 articles represent almost the equivalent in number to three years of publication by such an active government research center as Oak Ridge, or the number of papers released by the South's most active academic institution, the University of Texas, over a five-year span at current rates of productivity.[2]

No comparison is suggested in the quality of the research published, but there is a growing appreciation in liberal arts colleges for undergraduate research as a teaching tool, and for the satisfaction it brings to the instructor as a contributor to his own field of specialization.[3]

[3] EDITOR'S NOTE: See "Research and Teaching in the Liberal Arts College," a report of the conference on this theme held at the College of Wooster, June, 1959, under the sponsorship of the Division of Chemical Education with NSF support. Copies of this report are available from Dr. John D. Reinheimer, Department of Chemistry, College of Wooster, Wooster, Ohio, or Dr. Harry F. Lewis, Institute of Paper Chemistry, Appleton, Wisconsin.

✦ ✦ ✦

Proceedings of the

Pacific Southwest Association of Chemistry Teachers

Donald J. Cram
University of California,
Los Angeles

Recent Advances in Stereochemistry

A survey

In recent years, advances in our knowledge of molecular structure from spectral data coupled with the study of reaction mechanisms has inspired a renewed interest in the field of sterochemistry. Formerly, the "determination of structure" of an organic compound was considered complete when a structural formula could be written which indicated the sequence of atoms and bonds which composed the molecule. Now a three-dimensional representation is required before a structure is secured. Similarly, the early studies of organic reaction mechanisms were largely concerned with determinations of electrical type, and of molecularity. More recently, the subtle changes in molecular geometry which accompany chemical transformations are described in terms of three-dimensional formulas.

Of the large number of recent developments within the province of stereochemistry, possibly the following are the most important: (1) The absolute configurations of a large number of optically active compounds have been determined. (2) Correlations between configuration and rotation have been expanded and interpreted. (3) A host of conformational effects have been recognized and studied. (4) Factors which control asymmetric induction have been described. (5) Polymers containing many asymmetric carbon atoms have been prepared under conditions which produce highly ordered series of configurations. (6) The most highly strained members of molecular families have been prepared which demonstrate the limits which can be put on bond-angle deformations. (7) New types of molecular asymmetry due to restricted modes of internal motion have been reported. (8) The stereochemical courses of a number of chemical transformations have been elucidated.

The purpose of this article is to provide illustrations of these eight advances in sterochemistry, and to provide a glimpse of our state of knowledge of the field as a whole.

Absolute Configuration

In 1951, the Dutch chemists, Bijvoet, Peerdeman, and van Bommel (*1*) established through use of special X-rays the absolute configuration of molecules in a crystal of the sodium rubidium salt of (+)-tartaric acid. The configuration observed corresponded to that which had been assigned many decades earlier when the relative configurations of (+)-glyceraldehyde and (−)-tartaric acid were established. Fortunately, the absolute configuration of (+)-glyceraldehyde, and the configuration which had been arbitrarily given the molecule years before fortuitously corresponded to one another. Now the chemical world could assign absolute configurations to the large number of compounds whose configurations were known relative to that of (+)-glyceraldehyde. Since 1951 a large number of articles have appeared which report the absolute configurations of a host of natural products and synthetic materials(*2*). The group of compounds even includes some which owe their asymmetry to restricted rotation in substituted biphenyls(*3*).

Means of determining the relative configurations of asymmetric centers to one another have been expanded and refined in the last few years. Methods involving direct chemical interconversions have been supplemented with extensive correlations of sign of rotation and configuration, with asymmetric induction correlations (see next sections), and with phase diagram studies of "quasi racemates" (*4*).

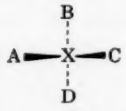
A notation for specifying absolute configuration has been suggested (*5*) which allows systematic names to be given to compounds which contain asymmetric centers, as well as to compounds that owe their asymmetry to restricted modes of internal motion. In this system, each asymmetric center is either *S* (sinister) or *R* (rectus), depending on the atomic weight and order of attachment of the four groups to the asymmetric center.

Correlations between Configuration and Rotation

The classic problem of correlating sign of rotation and configuration of optically active compounds has received considerable attention in recent years. In the steroid field, correlations based on additivity of rotary contributions of individual asymmetric centers to the rotation exhibited by the molecule as a whole have been developed (*6*). Correlations of long standing in the carbohydrate and terpene fields have been made compatible with one another, generalized, and extended (*7*). The optical rotatory dispersion technique has been developed by Djerassi (*8*), and has been used to determine the configuration of a large number of naturally occurring compounds.

Based on a paper presented at the PSACT Summer Conference on the Teaching of Chemistry, Asilomar, Calif., Aug. 19, 1959.

Perhaps the most ambitious attempt to devise a common basis for all correlations of sign and magnitude of rotation with configuration has been recently published by Brewster (*9*). This author makes use of a number of postulates: (1) a center of optical activity can be described as an asymmetric screw pattern of polarizability; (2) the four atoms attached to an asymmetric center (A, B, C, and D) can be ranked in orders of polarizability; (3) asymmetric atoms that possess configuration I are dextrorotatory when A > B > C > D in polarizability; (4) the magnitude of the rotatory contribution of an asymmetric center correlates with the amount of polarizability distributed in a screw sense about a center such as (I). This correlation



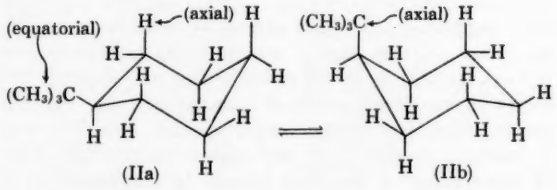
(I)

A>B>C>D
in polarizability

allows the sign of rotation to be calculated and the magnitude estimated for simple compounds free of conformational ambiguity. Application of the concepts of conformational analysis to more complex molecules allows the same calculations to be applied to a large variety of open-chain and cyclic compounds.

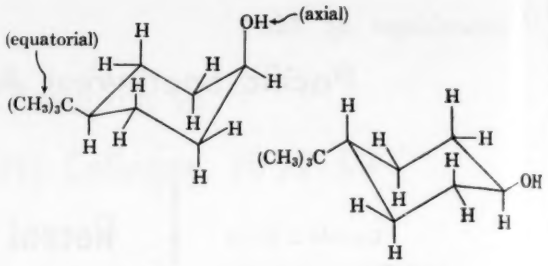
Conformational Analysis

One of the most important examples of the profits derived from the blending of organic and physical chemistry is found in the domain of conformational analysis. The early calculations of Pitzer and spectral investigations of Hassel led organic chemists to rational explanations for a large variety of observations pertaining to rates and equilibria that involve organic compounds (*10*). An example of the application of conformational analysis to six-membered rings illustrates the principles involved.



Of the two chair-forms of *tert*-butylcyclohexane (boat forms are too unstable to be considered), (IIa) is much more stable than (IIb) since there is much more room for the bulky *tert*-butyl group in the *equatorial* than in the *axial* position. Thus, the molecule can be treated as an essentially rigid system, with the *tert*-butyl group holding the molecule in conformation (IIa). When (IIa) is substituted in the 4-position with a hydroxyl group, two isomers can be prepared, (IIIa) and (IIIb), depending on whether the hydroxyl and *tert*-butyl groups are *cis* or *trans* to one another. Clearly the hydroxyl group is axial in (IIIa) and equatorial in (IIIb).

Two interesting questions concerning (IIIa) and (IIIb) can be settled by inspection of their structures: (*a*) which isomer is the more thermodynamically stable?



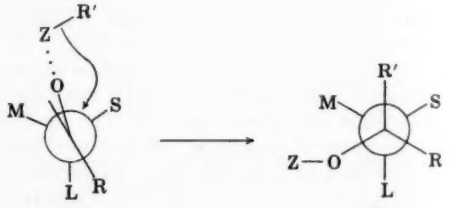
(IIIa)
cis, with OH axial

(IIIb)
trans, with OH equatorial

(*b*) which isomer reacts faster in esterification? Clearly (IIIb) is more stable than (IIIa) since the hydroxyl group is less hindered in the equatorial position (IIIb) than in the axial position (IIIa). For the same reason, (IIIb) undergoes esterification faster than (IIIa) (*11*).

Asymmetric Induction

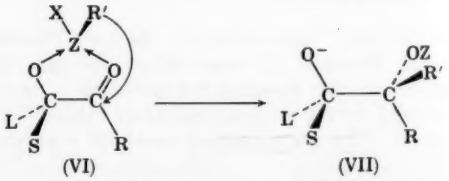
When a reaction is carried out in which a new asymmetric center is created in the presence of an old, the two diastereomers are not produced in equal amounts since the transition states leading to each isomer are sterically different, and of different energy. With certain types of reactions, the configuration of the predominant diastereomer can usually be predicted through use of either of two models (*12*). In the first of these, the old asymmetric center carries three substituents which can be labeled as large (*L*), medium (*M*), or small (*S*), depending on their size relative to one another. In this *open chain model*, these groups do not complex with the reagent employed to make the new asymmetric center, and (IV) produces (V) as the predominant product.



(IV)
Transition state
of lowest energy

(V)
Predominant
diastereomer

If on the other hand, the old asymmetric center carries a substituent such as a hydroxyl or amino group which is capable of complexing with the reagent, a rigid model such as (VI) applies. These models might be used to explain the steric course



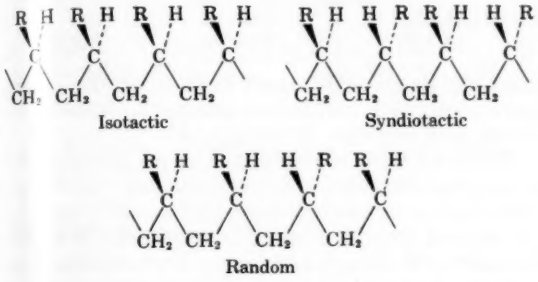
(VI)
Transition state
of lowest energy

(VII)
Predominant
diastereomer

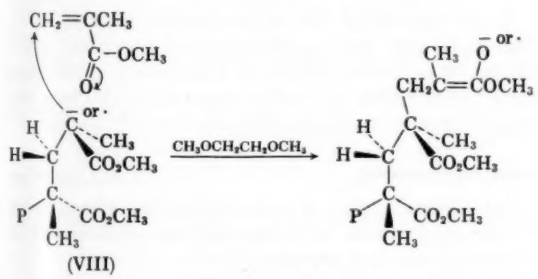
of reactions such as Grignard and hydride additions to carbonyl groups, and are useful in correlating and predicting configurations of diastereomers.

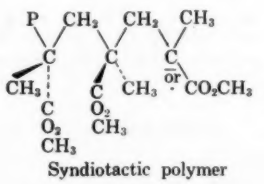
Asymmetric Induction in Polymerization

In synthetic polymers which contain asymmetric centers every third carbon atom, three types of configurational relationships have been realized, *isotactic*, *syndiotactic*, and *random* (*13*). Propylene polymerization with bimetallic catalysts (probably anionic) gives isotactic polymer (*14*). Anionic or radical polymerization

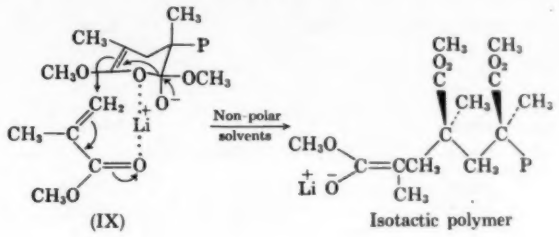


of methyl methacrylate in dissociating solvents gives syndiotactic polymer (*15*), whereas most polymerizations except when carried out under carefully controlled conditions give random polymer. The delicate balance of factors which controls the steric direction of these polymerizations is illustrated by the fact that methyl methacrylate can also be polymerized anionically to give isotactic polymer (*15*) by carrying out the reaction in non-dissociating solvents. Possible models for these stereospecific reactions are formulated (*12*).





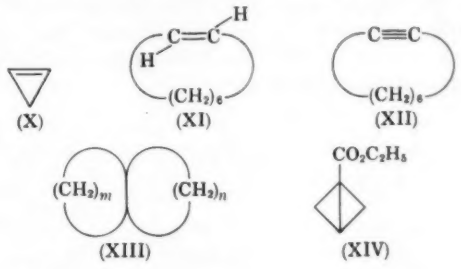
In (VIII), the growing polymer is depicted in a conformation which most exposes the carbanion or radical to attack, and which at the same time provides for the least internal steric compression within the chain. Presumably P > CO_2CH_3 > CH_3 in effective bulk. In (IX) a cyclic and semi-rigid model is formulated in which a six-membered ring is repeatedly made and destroyed at the end of the growing chain. The polymer chain and methoxyl groups occupy equatorial positions, and the ring is opened from the under side because in non-dissociating solvents, monomer coordinates with the metal cation of the ion-pair.



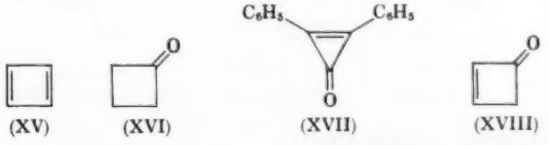
Strained Molecules

Much effort in recent years has been devoted to determining the point at which in homologous series of cyclic compounds, synthetic schemes fail due to an accumulation of steric strains. This type of work is important since it defines the boundaries of the structural theory of organic chemistry with respect to bond angle deformations and van der Waals compressions.

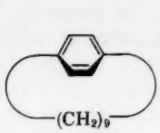
The smallest ring found to accommodate a *cis*-double bond is three-membered (*16*), a *trans*-double bond is eight-membered (*17*) as in structures (X) and (XI), respectively. Both of these compounds show abnormal reactivity, as does the smallest ring made which contains a carbon-carbon triple bond (XII) (*18*). A derivative of the smallest member of the homologous series, (XIII), compound (XIV), has recently been synthesized (*19*), and found to possess unusual properties. Cyclobutadiene (XV) has also now been reported, although its reactivity was so high that isolation and characterization in the normal manner proved impossible (*20*). Cyclobutanone (XVI) is the smallest

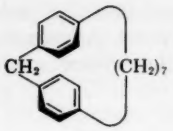


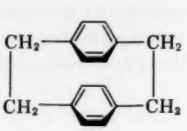
saturated cyclic ketone that has been reported (*21*), although diphenylcyclopropenone (XVII) has been synthesized (*22*). Cyclobutenone (XVIII) has also been synthesized recently (*23*), and possesses high reactivity.

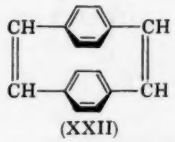


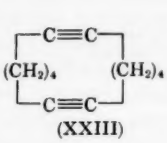
Compounds (XIX)–(XXIV) have now been synthesized, and are the smallest rings in their molecular families that have been prepared (*24*). Chances are high that lower homologues of (XIX) and (XXIII) will be synthesized in the future.

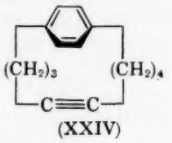

(XIX)


(XX)

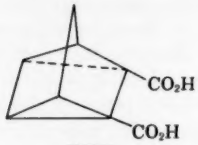

(XXI)

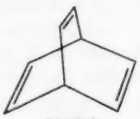

(XXII)


(XXIII)


(XXIV)

In the bicyclic field, a number of highly strained, but simple molecules have been reported, of which (XXV) (*25*) and (XXVI) (*26*) are possibly the most interesting.

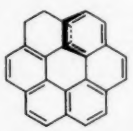

(XXV)


(XXVI)

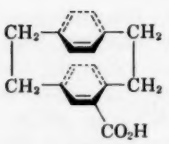
New Types of Molecular Asymmetry

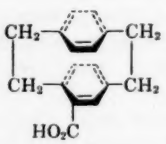
Aside from the classic examples of the optically active biphenyls (*27*) few compounds have been described which owe their molecular asymmetry to stereically restricted modes of internal motion. Two new types of compounds exhibit such asymmetry, and (XXVII) (*28*) and (XXVIII) (*29*) are examples. Enantiomers (XXVIIa) and (XXVIIb) are shaped like one turn of a helix, with the outer portions of the terminal benzene rings lying over one another. These rings cannot pass each other, and therefore the enantiomers are stable with respect to one another. Similarly (XXVIIIa) and (XXVIIIb) are prevented from equilibrating with one another because there is insufficient space to allow the benzene ring carrying the carboxyl groups to turn over.

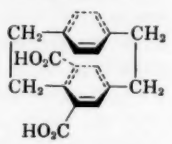
(XXVIIa)
Asymmetric


(XXVIIb)
Asymmetric

Coronene
symmetric
(page is one of seven
mirror planes)


(XXVIIa)
Asymmetric

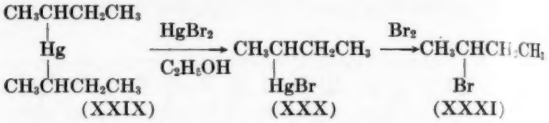

(XXVIIIb)
Asymmetric


Symmetric
(page is mirror plane)

Dynamic Stereochemistry

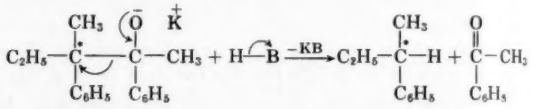
The mechanisms of most organic reactions can be reduced to substitutions, additions or eliminations, or combinations of these three fundamental transformations. The sterochemistry of simple examples of these reactions has been extensively studied and reviewed (*30*), and only two of the more recent investigations will be discussed here.

The neglected field of electrophilic substitution at saturated carbon (S_E reaction) has only recently received the attention it deserves. Organomercury compound (XXIX) has been obtained in an optically pure state, and submitted to the reactions indicated (*31*), both of which proceeded with high (possibly complete) retention of configuration at the carbon atom undergoing substitution. The first of these reactions was demonstrated (*31b*) to be bimolecular (S_E2) in mechanism.


(XXIX) (XXX) (XXXI)

Since the electrophilic attack must be on the bonding pair of electrons, it is not surprising that substitution occurs with retention of configuration.

Reactions which belong to the monomolecular variety of electrophilic substitution at saturated carbon have been studied in many systems (*32*) in which carbon is the leaving group. These transformations have been demonstrated to involve carbanion intermediates, which go to product with high retention, complete racemization or high inversion, depending on the symmetry properties of the solvent envelope. Typical results are:

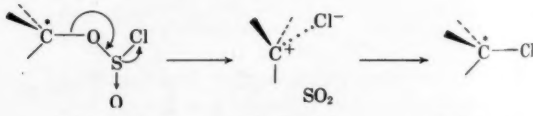


Solvent (H-B)	Stereochemical outcome
$(CH_3)_3COH$	93% net retention
$(CH_3)_2SO$	complete racemization
$HO(CH_2CH_2O)_2H$	60% net inversion

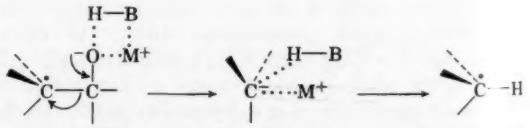
A comparison of the stereochemical courses of the monomolecular nucleophilic and electrophilic substitutions at saturated carbon is instructive, particularly since the patterns of results obtained in the two electronic varieties of substitution reactions are similar.

Retention Mechanism

S_N1—Occurs when a complex leaving group carries its own nucleophile, as in the reactions of chlorosulfites in non-dissociating solvents.

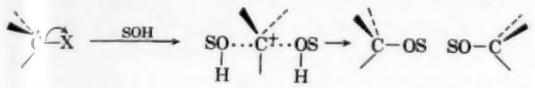

Alkyl sulfite — Asymmetric ion pair — Retained configuration

S_E1—Occurs when complex leaving group carries its own electrophile, as in reactions of alkoxides in non-dissociating solvents.


Solvated metal alkoxide — Asymmetric ion pair — Retained configuration

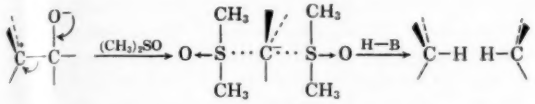
Racemization Mechanism

S_N1—Occurs in relatively non-nucleophilic but strongly dissociating solvents in which relatively long-lived carbonium ions react with external nucleophiles.



Alkyl halides, tosylates, etc. | Symmetrically solvated carbonium ions | Racemic product

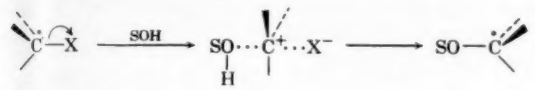
S_N1—Occurs in non-proton donating but strongly dissociating solvents in which relatively long-lived carbanions react with external electrophiles.



Alkoxide anions or solvent-separated ion pairs | Symmetrically solvated carbanions | Racemic product

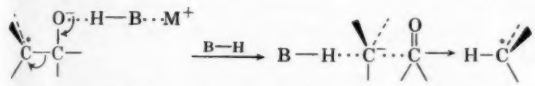
Inversion Mechanism

S_N1—Occurs in strongly-nucleophilic and ionizing solvents in which short-lived carbonium ions react with external nucleophiles.



Alkyl halides, tosylates, etc. | Asymmetric ion pair | Inverted configuration

S_E1—Occurs in strongly-electrophilic and dissociating solvents in which short-lived carbanions react with external electrophiles.



Solvent-separated ion pair | Asymmetrically solvated carbanion | Inverted configuration

Literature Cited

(1) Bijvoet, J. M., Peerdeman, A. F., and van Bommel, A. J., *Nature*, **168**, 271 (1951).

(2) Many examples are listed by Mills, J. A., and Klyne, W., "Progress in Stereochemistry," Vol. I, Butterworths Scientific Publications, **1954**, pp. 172–222.

(3) E.g., Mislow, K. and McGinn, F. A., *J. Am. Chem. Soc.*, **80**, 6036 (1959) and Gerson, J. A., and Greenbaum, M. A., *Ibid.*, **80**, 445 (1958).

(4) Klyne, W., "Progress in Stereochemistry," Butterworths Scientific Publications, London, **1954**, pp. 201. E.g., Fredga, A., *Arkiv. Kemi Mineral Geol.*, **15B**, No. 23 (1942) and Fredga, A., and Miettinen, J. K., *Acta. Chem. Scand.*, **1**, 371 (1947).

(5) Cahn, R. S., Ingold, C. K., and Prelog, V., *Experientia*, **12**, 81 (1956).

(6) Klyne, W., "Progress in Stereochemistry," Butterworths Scientific Publications, London, **1954**, p. 209.

(7) Bose, A. K., *J. Org. Chem.*, **20**, 1003 (1955).

(8) Djerassi, C., "Optical Rotatory Dispersion. Applications to Organic Chemistry, McGraw-Hill Book Co., New York, **1960**.

(9) Brewster, J. H., *J. Am. Chem. Soc.*, **81**, 5475 (1959). This author's work was to some extent anticipated by D. H. Whiffen (*Chem. and Ind.*, 964 (1956)), who developed a limited correlation based on patterns of polarizability of groups attached to asymmetric centers.

(10) The field has been extensively reviewed: (*a*) Dauben, W. G. and Pitzer, K. S., in Newman, M. S., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, **1956**, pp. 3–60; (*b*) Barton, D. H. R., and Cookson, R. C., *Quarterly Reviews*, **10**, 44 (1956).

(11) Winstein, S. and Holness, N. J., *J. Am. Chem. Soc.*, **77**, 5562 (1955).

(12) Cram, D. J., and Kopecky, K. R., *J. Am. Chem. Soc.*, **81**, 2737 (1959).

(13) Stille, J. K., *Chem. Revs.*, **58**, 541 (1958).

(14) Natta, G., *Gazz. Chimi. Itali.*, **89**, 89 (1959).

(15) Fox, T. G., et al., *Gazz. Chimi. Itali.*, **80**, 1769 (1958).

(16) (*a*) Demjanov, N. J., and Dojarenko, M., *Ber.*, **56**, 2200 (1923); (*b*) Schlatter, M. J., *J. Am. Chem. Soc.*, **63**, 1733 (1941).

(17) Ziegler, K., and Wilms, H., *Ann.*, **567**, 1 (1950).

(18) Domnin, N. A., *J. Gen. Chem.* (U.S.S.R.), **8**, 851 (1938).

(19) Wiberg, K. B., and Ciula, R. P., *J. Am. Chem. Soc.*, **81**, 5262 (1959).

(20) Avram, M., Nenitzescu, C. D., and Marica, E., *Ber.*, **90**, 1857 (1957).

(21) Roberts, J. D., and Sauer, C. W., *J. Am. Chem. Soc.*, **71**, 3925 (1949) and references quoted here.

(22) Breslow, R., Haynie, R., and Mirra, J., *J. Am. Chem. Soc.*, **81**, 248 (1959).

(23) Vogel, E., Private communication.

(24) Cram, D. J., *Record Chem. Progr.*, **20**, 71 (1959).

(25) Cristol, S. J., and Snell, R. L., *J. Am. Chem. Soc.*, **80**, 1950 (1958).

(26) Zimmerman, H. E., and Paufler, R. M., *J. Am. Chem. Soc.*, **82**, 1514 (1960).

(27) Shriner, R. L., Adams, R., and Marvel, C. S., in Gilman, H., "Organic Chemistry," John Wiley and Sons, Inc., **1943**, pp. 343–82.

(28) Newman, M. S., Luty, W. B., and Lednicer, D., *J. Am. Chem. Soc.*, **77**, 3420 (1955).

(29) Cram, D. J., and Allinger, N. L., *J. Am. Chem. Soc.*, **77**, 6289 (1955).

(30) Newman, M. S., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, **1956**, pp. 61, 201, and 304.

(31) (*a*) Jensen, F. R., et al., *J. Am. Chem. Soc.*, **81**, 1262 (1959). (*b*) Charman, H. B., Hughes, E. D., and Ingold, C. K., *J. Chem. Soc.*, 2523 (1959).

(32) Cram, D. J., et al., *J. Am. Chem. Soc.*, **81**, 5774 (1959).

NEACT Twenty-Second Summer Conference August 22–27, 1960, University of Maine, Orono

For complete program and registration details write:
the Conference Secretary, Maurice Bernier,
Farmington High School,
Farmington, New Hampshire.

Report of the New England Association of Chemistry Teachers

Walter C. Weber
Burgess Fobes Paint Company
Portland, Maine

Chemicals in the Manufacture of Paint

Every homeowner or basement hobbyist knows that paint is a mixture. The need for thorough stirring tells him this. Also, the wide difference in the performance of various formulations tells him that paint is not a random mixture but is a carefully selected blend of specific ingredients. Each of these has been added with a definite purpose in mind. Paintmaking began as an art, but in recent years the chemist has entered the field and is bringing a measure of understanding to the many complicated problems involved. As a result of his studies, many new substances with valuable new properties have been introduced to the industry. Today, the field of paint chemistry is one which is moving rapidly forward in many different directions.

Reduced to simplest terms, a paint consists of a vehicle, a drier, and a pigment. Linseed oil is the traditional vehicle, although for various reasons—economic as well as chemical—it is now commonly mixed with other oils. In terms of composition, these oils are glycerol esters of unsaturated long chain fatty acids. The "drying" of such oils is not evaporation but is a hardening by polymerization and atmospheric oxidation at the carbon to carbon double bonds. Thus the number and the location of the double bonds in the acids is significant. As would be predicted, esters of saturated fatty acids are non-drying oils. They cannot take up oxygen and hence remain liquids, even after months of exposure to air. "Driers" are substances which accelerate the oxidation and polymerization change. They are usually the oxides or organic salts of such metals as cobalt, manganese, lead, or zinc. These substances form compounds with the oils, affect the rate of hardening, and impart specific properties to the resulting film. There are special requirements for the pigment, too. It must be opaque if it is to have good hiding power, a factor of importance because the greater the hiding power the smaller the amount of paint needed to cover a given surface. The pigment should mix well with the oil, be inert while the paint is protected from the atmosphere, be inert to gas impurities like hydrogen sulfide after exposure to the atmosphere, and should preferably be non-poisonous. A good pigment provides protection as well as imparts color.

The mode paint manufacturer uses pigments, vehicles, and driers which together give the best chemical and physical characteristics to the final product. For example: Paints for outside use are formulated with pigment and vehicle so that the dry film is from 28 to 32% pigment by volume. In trim paints and outdoor enamels concentration of pigment by volume runs from 5-20% of the dry film, depending on the color and type of finish.

Pigments

In a house paint, the two white leads (basic carbonate and basic sulfate), leaded zinc oxide, zinc oxide, titanium dioxide, and to a certain extent antimony oxide are used exclusively, mixed with extender pigments like magnesium silicate, barytes, mica, silica, and whiting. The chemically-active pigments of this group are the white leads and the zinc pigments.

A balance of pigments is necessary to give a durable finish. White lead gives a certain flexibility to the film due to the formation of lead soaps when the active part of the white lead particle ($Pb(OH)_2$) reacts with the fatty acids of the linseed oil. Zinc oxide reacts to a lesser or greater extent, depending on its particle size, but forms a soap which tends to give hardness to the film. Free calcium oxide in whiting reacts with the fatty acids of linseed oil to impart brittleness. Mica is inert, but floats to the top of a wet paint film, and gives some protection in a physical way. Magnesium silicate is a fibrous extender and imparts physical flexibility.

Climatic conditions have a definite influence on the durability of a paint film. In the New England area, a typical pigment combination for a best grade white house paint would be 47% leaded zinc with 53% titanium dioxide and extender pigment. This combination would give 32% zinc oxide, 17% basic lead sulfate, 26% titanium dioxide, and 25% magnesium silicate.

Today, titanium dioxide is manufactured from a natural ore, ilmenite, which is an iron titanate soluble in sulfuric acid. Naturally occurring rutile runs about 98% TiO_2, but it is not acid-soluble. Ilmenite occurs as a sea sand in India, in the Rockfish Valley of Virginia, in New York, and in Canada. It is shipped as a concentrate, with the Indian product running about 52%

Presented at the 302nd Meeting of the New England Association of Chemistry Teachers, October 10, 1959, at the Gorham State Teachers College, Gorham, Maine.

TiO_2, the Virginia product about 42%, and the Canadian variety about 60%. The acid solution temperature of the ilmenite ore is lowered to remove ferrous sulfate by crystallization. Then the solution is diluted with water to give a titanium sulfate cake which is calcined. A chloride process in which titanium tetrachloride is formed is now used successfully. This process is said to give a superior type of pigment which can be dispersed in paint vehicles by means of roller or pebble mills. High speed mixers of 1300 rpm give excellent dispersions.

Suitable magnesium silicate occurs naturally in upper New York State. Because a uniform particle is required for house paints, it is finely ground so that 98.5% of it will pass through a 325-mesh sieve.

For marine enamels and trim paints, chrome yellow and chrome green pigments are used. An orange pigment based on the coprecipitation of lead molybdate and chromate gives a very durable pigment having more opaqueness than the chromate. Ordinarily, as much as five pounds of lead chromate per gallon of enamel would be required to make a satisfactory yellow enamel. By using lead molybdate pigment this can be reduced, depending on the shade, to as little as three pounds per gallon of enamel. The resulting enamel has higher gloss, better flow, and the settling is less.

In toy enamels applied by tumbling, dipping, spraying, and brushing, the requirement for pigments is not so rigid as for outdoor trim enamels, or for floor, deck, and marine enamels. However, certain non-toxic requirements must be met. Such enamels cannot contain lead, arsenic, antimony, cadmium, or mercury in any form. The American Standards Association has recently banned the use of barium. Barium lithol was a very bright popular red, made by the diazotization of tobias acid, coupled with beta naphthol. The substitute used is a combination of benzidene yellow and calcium lithol. Benzidene Yellow does not have the opaqueness of lithol and costs more than twice as much. For greens, mixtures of Prussian Blue and Benzidene Yellow are used, and for orange, dinitraniline orange toner.

Oils

Five oils are used today in large quantities for vehicles and vehicle manufacture. These are linseed, soya, tung, dehydrated castor, and, to a more limited extent, safflower oils.

Linseed oil has the necessary chemical characteristics for the manufacture of house paints. A typical analysis would give linoleic acid, 40%, linolenic acid, 35%, oleic acid, 15%, stearic acid, 5%, and the glyceryl radical, about 5%. From the table it may be seen that linolenic acid has three double bonds and linoleic acid has two. These are the fatty acids which facilitate drying. Oleic acid with only one double bond and stearic acid with none are "non-drying" acids.

Tung, or Chinawood Oil, is the fastest drying, oil, but it should be used only when properly cooked with resins. A typical analysis would read: eleostearic acid, 72.8%, oleic acid, 13.6%, palmitic acid, 3.7%; stearic acid, 1.2%; and the glyceryl radical, 4.4%. Thus the major acid of this oil is eleostearic acid, an isomer of linolenic acid having its three double bonds in a slightly different location.

Table 1. Fatty Acids Important in Paint Manufacture

Stearic acid	$CH_3(CH_2)_{16}COOH$
Oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
Linoleic acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
Linolenic acid	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
Eleostearic acid	$CH_3(CH_2)_3CH{=}CHCH{=}CHCH{=}CH(CH_2)_7COOH$
Licanic acid	$CH_3(CH_2)_3CH{=}CHCH{=}CHCH{=}CH(CH_2)_7CO(CH_2)_2COOH$

Oiticica oil is sometimes used as a tung oil replacement. In varnish production it is often considered to have the physical properties of a mixture of tung and linseed oils. Its major constituent is licanic acid, a derivative of eleostearic acid having a keto group on the fourth carbon.

Alkyd Resins

Enamel formulation includes the use of alkyd- and varnish-type vehicles. This type material is also referred to as "Glyptal," a name which is taken from the words "glycerine" and "phthalic acid."

Alkyds generally are purchased from the chemical manufacturers as solutions in mineral spirits, xylol, toluol, or other solvents. If the paint manufacturer wishes to manufacture an enamel using only mineral spirits as the solvent, he is limited in the type of alkyd available. A maximum of 35% phthalic anhydride with soya and linseed oils can be used with glycerine, pentaerythritol, or other alcohols to give a polymerized product soluble in mineral spirits. If combinations of xylol, toluol, and a petroleum solvent are used, up to 40% phthalic anhydride may be chemically combined. High phthalic anhydride content gives faster drying alkyds, better gloss retention for outside enamels, and chemical resistance to oils, greases, and staining. After proper curing enamels based on this type alkyd are gasoline proof.

Alkyds are considered to have the best gloss retention when used as a clear finish. They have equalled or outperformed the newer synthetics like the epoxies and the polyurethanes. In general, they have better gloss retention than the phenol formaldehyde varnishes, but they do not have as good alkali resistance. The resistance can be improved by the addition of chlorinated rubber. This rubber comes as a white powder which is 67% chlorine by weight. It is soluble in xylol and may be added to alkyds in xylol solution. Alkyds based on soya bean oil of 23% phthalic acid content are also miscible with this rubber.

For greater chemical resistance, the alkyds cannot be used. Chlorinated bi-phenyls must be used as plasticizers. Unfortunately these finishes are not oil-resistant and soften readily with solvents. For ultimate alkali resistance the styrene-butadiene copolymers are used. They will resist 50% caustic soda; however, the adhesion to metal surfaces is poor and the film hardness is low. They also require a proportion of aromatic solvent in the vehicle.

Fire-retardant paints are paints that do not burn or afterglow on direct fire. Alkyds with chlorinated rubber make good fire-retardant vehicles. A vehicle consisting of 47% of a chlorinated dibasic acid in which the chlorine content of the dibasic acid is 52% and the oils

acids 45% is an excellent fire retardant vehicle. The pigments generally used are titanium dioxide, calcium carbonate, antimony oxide, barium sulfate, and magnesium silicate. Chlorinated paraffin wax containing 70% chlorine is a white powder. When in partial solution in mineral spirits this powder can be used with alkyd solutions to give a fire-retardant vehicle. The amount used is between 35 and 50% of the alkyd solids.

Other Varnishes

In varnish manufacture the first varnishes made that would dry overnight were based on formulations of limed-rosin and tung oil. Rosin, which is largely abietic acid can be reacted with lime, CaO, to 6% by weight at a temperature of about 480°F. Tung oil is then polymerized at a slow rate controlled by the acid character of the resin. Ester gum-tung oil varnishes were the first "four-hour" varnishes.

An excellent varnish is one based on an oil soluble paraphenyl formaldehyde resin and tung oil. A formulation of two parts tung oil and one part resin will have good alkali resistance for 48 hours in a 5% sodium hydroxide solution. A varnish of this type requires only mineral spirits as a solvent, has a good outdoor durability, will dry in about four hours, and can be used as a general utility varnish or for the manufacture of certain acid and alkali-resisting enamels.

Alkyds are often fortified with melamine to give baking finishes. Styrenated alkyd gives very fast drying vehicles. Epoxies, based on reactions of bis-phenol and epichlorhydrin have exceptional adhesion to metal surfaces and the best resistance to acids and alkalies. Polyurethanes do not dry as fast as the styrenated alkyds, but have slightly better gloss retention outdoors, and have more alkali resistance than alkyds.

A good many vehicles today used for lower priced manufactured paint are based on tall oil. Tall oil in this country is supplied as a by-product of the paper industry. The refined tall oil runs approximately 45% rosin acids, 43% fatty acids, and 6% sterols. The dominant fatty acid is linoleic. When this material is cooked with glycerin or other alcohol, the esterified product in mineral spirits gives a drying varnish comparable to a 50% ester gum-linseed oil varnish. Rosin acids are sometimes treated with zinc oxide. A resin containing 6–8% zinc (as metal) can be used as a modifying resin to give better flow and gloss to certain alkyds, petroleum, and cumar resin varnishes.

Acrylic Polymers

For good chemical resistance, formulations are often made using solutions of acrylic ester polymers in xylol, toluol, or methyl ethyl ketone. These polymers are water white, dry very fast, but require plasticizers like butyl benzyl phthalate or some modified polyester resins.

The acrylics are used extensively in emulsion form today. Polyvinyl acetate is also used in large quantities. Insufficient time has elapsed to conclude which emulsion is superior. So far, the acrylic type seems to have the better flexibility. The cost of production has been reduced sufficiently so that any quality advantage would mean that the acrylic resin will be used in larger quantities.

Emulsions are used only over oil primers on wood, and if old paint is in a very chalky state, an oil primer must still be used. In some cases acrylic emulsions or polyvinyl acetate emulsions may be modified with oil alkyds and used over painted surfaces. Emulsion paints have made good masonry paints.

Driers

Metal derivative driers and drier catalysts are generally of the naphthenate type. Cobalt drier is a purple solution of cobalt naphthenate in mineral spirits. The resulting solution is generally 6% cobalt on the weight basis. Lead drier is generally 24% lead, and manganese drier is 6%. All drying vehicles dry in proportion to the metal content added.

Drier catalysts including zirconium, iron, and calcium are used in conjunction with cobalt for baking vehicles. Lead naphthenates sometimes form insoluble lead phthalate when used with alkyds, and calcium prevents the precipitation of the lead to give improved drying.

The metal tallates based on tall oil are often used for economy, but like the metal linoleates they oxidize and are not stable. The metal octoates (metallic salts of 2-ethyl hexoic acid) are used in odorless petroleum solvents to give drier solutions for use in odorless paint systems.

The term "boiled" linseed oil is a misnomer. Actually, this is a refined linseed oil in which lead in the form of litharge and manganese as the linoleate are reacted with linseed oil at about 450°F. At this temperature the litharge reacts to form lead linoleate and the manganese linoleate goes into solution in the oil. Bubbles are formed as small amounts of steam are given off and as minute particles of vegetable tissues undergo destructive distillation. This gives the appearance of boiling. The product is a faster drying oil, but it is in no way polymerized as one would expect from the name.

Conclusion

It should be apparent from this brief survey that the chemist has had a most effective hand in bringing the paint industry to its present active state. Of necessity, most of our attention has been devoted to products and processes which were unknown or not understood a few short years ago. The consumer, with his demand for quick-drying finishes, for chemical-resistant finishes, for one-coat paints, and for odorless paints has made the manufacture of these products into a most competitive field. With the demand continuing and with the paint chemists striving to meet it, who can predict what will be in the future? Right now, however, our present-day finishes provide beauty and protection for the structural and finish materials of our civilization. They make our world with its damp, corroding atmosphere into a brighter, healthier, easier, and less expensive place in which to live.

+ + +

Chem Ed

BOOK REVIEWS

A Modern Approach to Organic Chemistry

J. Packer and *J. Vaughan*, both of University of Canterbury, Christchurch, New Zealand. Oxford University Press, New York, 1958. x + 973 pp. 16.5 × 24.5 cm. $13.45.

Whether he may decide to adopt this book as a text or not, every instructor responsible for a first year course in organic chemistry will find it different enough, in comparison with American texts, to warrant a careful examination. Almost all new texts for the introductory course in organic chemistry which have been published in the past decade have shared the objectives stated in the preface to this one, "to present side by side factual material and theoretical ideas"; however, there are no more than three or four American texts which have made as thorough an incorporation of the theoretical framework with the introductory stages of organic chemistry.

Since these books are of a new genre and their authors are experimenting with a new presentation of organic chemistry, it seems inevitable that they will suffer in common from such pitfalls as oversimplification, the inclusion of too much material for the beginning student, and an occasional erroneous or outdated theoretical construction. With respect to these difficulties this text comes off well with the best three or so American texts. It compares most favorably in the illustrations cited from the original literature as background for understanding the commonly held mechanistic ideas and perhaps less favorably with respect to the number of rather rash guesses suggested for mechanisms which are not clearly understood as yet.

A book of this type can be used for course instruction most effectively if, as suggested by C. K. Ingold in the foreword, "... the organic chemical teacher must know the physical theory so well that he is able to introduce it to elementary students in statements that are satisfyingly simple and yet strictly correct..."

If Ingold's admonition concerning statements being strictly correct had been applied more rigorously, several of the less propitious selections of illustrative material would have been improved. For example, on page 56 there occurs the expression:

$$H_2C = CH_2 \rightleftarrows H_2\overset{+}{C} - \overset{-}{C}H_2 \xrightarrow{\text{etc.}}$$

While the outline of homolytic and heterolytic mechanisms is fully qualified and quite adequately explained on subsequent pages, I expect that the average not-too-critical student will, in spite of forceful warning to the contrary, simply recall this and use it as an erroneous notion of a kind of ionization long after he has forgotten the written and verbal explanations.

While Chapter 15 presents a very good discussion of substitution in benzene in terms of the intermediate ion or radical, the discussion of the reactions of substituted benzene in Chapter 16 very nearly ignores the effect of substituents on the stability of alternative transitory ions and thus is not in keeping with the level of discussion maintained in the earlier chapters.

Although the acidity of carboxylic acids (pp. 249–50) is explained in terms of the relative stabilities of the ion and acid, the explanation of the acidity of phenol (p. 699) ignores the resonance stabilization of the ion, and the effect this has on the equilibrium; however, this is an error shared by all but two of the current organic texts.

In spite of these adverse comments on those presentations which could be improved, I feel that this book has much to recommend it. Many of the discussions of the mechanisms of reaction of important functional groups carry references to the historical development of these ideas and to key experiments which were used to establish our present understanding. All of the mechanistic sequences are clearly illustrated with electron dot formulas where they are significant. With the exceptions noted above, the general level of discussion throughout the book is distinctly more complete and coherent than is found in the majority of textbooks for introductory organic chemistry.

As is customary with Oxford Press books, this one is typographically excellent with clear, easy-to-read type; however, it suffers in one respect from the high quality of paper used. It is within a few pages of being the same length as several widely-used American texts; however, since it is printed on bulking paper in place of the heavily calendered paper generally used, it is a full 3 inches thick compared to 2 inches for the usual printing of books of this pagination.

MARSHALL W. CRONYN
Reed College
Portland, Oregon

Organic Chemistry

Donald J. Cram, University of California at Los Angeles, and *George S. Hammond*, California Institute of Technology, Pasadena. McGraw-Hill Book Company, Inc., 1959. xv + 712 pp. Figs. and tables. 17 × 24 cm. $8.50.

Late in the nineteenth century a textbook on organic chemistry was written by Ira Remsen. At the time this book was quite revolutionary for, for the first time, organic compounds were classified, and their reactions discussed according to the nature of the functional group which was present. The revolutionaries have now been in power for over seventy years—so long, in fact, that some might even call them reactionaries.

In 1959 Cram and Hammond wrote an organic text which may well start another revolution, and is at the very least certain to start an argument. Traditionally, organic chemists have been concerned primarily with the initial and final states—what are the properties of compounds and how may one compound be converted into another? The past thirty years have seen the emphasis shift to one of trying to understand how reactions take place—by what path or mechanism do molecules react? Briefly then, the Cram and Hammond approach is not to classify organic reactions according to the nature

Reviewed in This Issue

J. Packer and J. Vaughan, A Modern Approach to Organic Chemistry

Donald J. Cram and *George S. Hammond*, Organic Chemistry

Roger Adams, Editor-in-Chief, Organic Reactions, Volume 10

Eugene Galanter, Editor, Automatic Teaching: The State of the Art

E. B. Sandell, Colorimetric Determination of Traces of Metals

William D. Kingery, Editor, Kinetics of High-Temperature Processes

H. Eyring, Editor, *C. J. Christensen* and *H. S. Johnston*, Associate Editors, Annual Review of Physical Chemistry. Volume 10, 1959

Olaf A. Hougen, Kenneth M. Watson, and *Roland A. Ragatz*, Chemical Process Principles. Part 2: Thermodynamics

Keith Gordon Irwin, The Romance of Chemistry

William D. Kingery, Property Measurements at High Temperatures

Cecil L. Wilson and *David W. Wilson*, Editors, Comprehensive Analytical Chemistry. Volume 1A: Classical Analysis

Jean Timmermans, The Physico-Chemical Constants of Binary Systems in Concentrated Solutions. Volume 3: Systems with Metallic Compounds.

Milan Bier, Editor, Electrophoresis: Theory, Methods and Applications.

of the functional group, but rather to classify reactions according to the mechanism involved. Such an approach is not unusual in advanced texts but this is probably the first time it has been tried in a book designed for students who are getting their initial exposure to organic chemistry.

The first four chapters of this text are devoted to vocabulary in the classical sense, namely, nomenclature of the different classes of organic compounds along with some methods of synthesis and a few reactions. The latter are selected carefully, primarily to illustrate methods of structure proof (for example, the Kuhn-Roth C-methyl determination) and no attempt is made to teach the whole of organic chemistry at this stage.

The next four chapters deal with structure and physical properties. The nature of the covalent bond is discussed and the concept of resonance is introduced. Once the student has been provided with a firm foundation of molecular geometry the important features of stereochemistry (including conformational analysis) are treated. This early introduction of stereoisomerism is one of the many excellent features of this book. It is extremely important that future organic chemists be brought face to face with this phenomenon early in the game, not only because changes in stereochemistry often provide important clues to mechanism, but also because most practical problems of synthesis today are not just how to reduce a ketone to an alcohol but rather how to get the alcohol with the desired configuration.

The meat of the text is incorporated in Chapters 9 through 20. Here the reactions of organic chemistry are discussed in terms of mechanism. Chapters are devoted to nucleophilic and electrophilic substitution at saturated and unsaturated carbon atoms, to nucleophilic and electrophilic additions, elimination reactions, free-radical reactions, oxidation-reduction reactions, and molecular rearrangements. One should not worry about the exclusion of reactions useful in synthesis. All the reactions one could wish for are there; in fact, if anything there is too much in this section. While the central theme is mechanism, synthetic applications are emphasized repeatedly with many examples drawn from the literature. This reviewer was particularly pleased to see per cent yields reported for most of the reactions used; everybody (except the poor undergraduate) knows that the Wurtz reaction is a mighty poor way to prepare a hydrocarbon but Cram and Hammond say so. The many problems at the end of each chapter are nothing short of magnificent. They will make the student think and, with any sort of luck will drive him into the original literature. On the whole, though, this reviewer would have preferred seeing fewer reactions covered but with a greater wealth of experimental evidence cited in support of the mechanisms postulated.

The final section of this book consists of some nine chapters on special topics such as polymers, heterocyclic compounds, carbohydrates, amino acids, alkaloids, steroids, etc. Particularly noteworthy here is a chapter on spectra and dyes in which is included an all too brief discussion of ultraviolet, visible, infrared and Raman spectra, and nuclear magnetic resonance absorption. There is also a very good chapter on the nomenclature of organic compounds and a slightly disappointing chapter on the literature of organic chemistry.

Many organic chemists will worry about this book for at least two reasons. Even now most organic reactions are performed with the purpose of obtaining a product and one can argue that the emphasis should therefore be on initial and final state rather than on mechanism. It must be re-emphasized, however, that Cram and Hammond's book does not slight synthesis but does try to put it on a more rational basis. The other argument might be that while a reaction is a fact, a mechanism is often something considerably less substantial and hence it might be unwise to build on such a relatively flimsy foundation. Here each reader must use his own judgment but it appears to this reviewer that it is worth some risk to try to ease the burden of memorization which is so often the lot of the organic chemist.

A much more serious problem is the nature of the laboratory work which might be used along with a text such as this. Briefly, the question is "How are you going to keep 'em down on the farm, after they've seen Paree?" Instructors must devise experiments which are not only of preparative value but which also have some theoretical and/or research significance. With freshman chemistry having reached the point where it is about 50 per cent physical chemistry many interesting experiments should be within the capabilities even of sophomores studying organic chemistry the Cram and Hammond way. Some might even want to prepare one of the "reported" compounds pictured on the front cover. Successful synthesis of the first of these ought to rate at least an 'A' in the course.

E. S. Graham
Kenyon College
Gambier, Ohio

Organic Reactions, Volume 10

Roger Adams, Editor-in-chief, University of Illinois, *et al.* John Wiley & Sons, Inc., New York, 1959. vii + 563 pp. Many tables. 15.5 × 23.5 cm. $12.

The quality and usefulness of each volume in this well-known series have long been acknowledged by all chemists concerned with organic reactions. This new volume, especially the chapter reviewing the Michael Reaction, is a welcome addition to an indispensable series.

In all three chapters the literature is reviewed through 1955, although a few references of more recent date have been included. This literature lag, due to publication delays and to delayed arrival of *Chemical Abstracts* subject indexes, has become a serious problem for authors of review articles.

The chapters included in this volume are:

(1) The Coupling of Diazonium Salts with Aliphatic Carbon Atoms, by Stanley M. Parameter; 142 pages, 541 references, 101 pages of tables. Coverage is limited to those reactions in which both nitrogen atoms of the diazonium salt are retained in the resulting molecule.

(2) The Japp-Klingemann Reaction, by Robert R. Phillips; 36 pages, 120 references, 16 pages of tables. Since the Japp-Klingemann reaction is a special case of coupling of diazonium salts with aliphatic compounds, Chapters 1 and 2 are complementary.

(3) The Michael Reaction, by Ernst D. Bergmann, David Ginsburg, and Raphael Pappo; 377 pages, 1065 references, 271 pages of tables. A prodigious undertaking, this chapter discusses not only donors and acceptors activated by carbonyl and carbalkoxyl groups but includes such donors as nitriles, nitro compounds, sulfones, and certain hydrocarbons as well as acceptors such as vinylsulfonium compounds, certain hydrocarbons, and unsaturated cyclic quaternary ammonium salts.

Robert K. Ingham
Ohio University
Athens, Ohio

Automatic Teaching: The State of the Art

Edited by *Eugene Galanter*, Center for Advanced Study in the Behavioral Sciences, University of Pennsylvania. John Wiley & Sons, Inc., New York, 1959. viii + 198 pp. Figs. 15 × 23.5 cm. $3.25.

This book is misnamed. There is no such thing as automatic instruction; there are only automated devices for presenting information, whether the automation is provided by an electric motor or the student himself.

The book is a collection of the papers presented at a conference held at the University of Pennsylvania in 1958, entitled "Conference on the Art and Science of the Automatic Teaching of Verbal and Symbolic Skills." The contents are 16 papers of very uneven value, divided between descriptions of experiments which have been better described elsewhere, and jargon-embroidered pronouncements on learning theory.

Nonetheless, the book is a landmark in the sense that it is the first book published dealing entirely with this important and rapidly developing field. It will serve a real and valuable function in providing those in the field of automated instruction, and in psychology, with a discussion (however incomplete) of ideas and re-evaluations, though there is little or no new information. It does demonstrate the widely held conviction that teaching methods can be improved, as it shows the diversity of opinion as to means.

If one is already engaged in teaching machine experimentation, the book is worth while; if one is not, this book is not the place to begin.

Jesse H. Day
Ohio University
Athens, Ohio

(*Continued on page A380*)